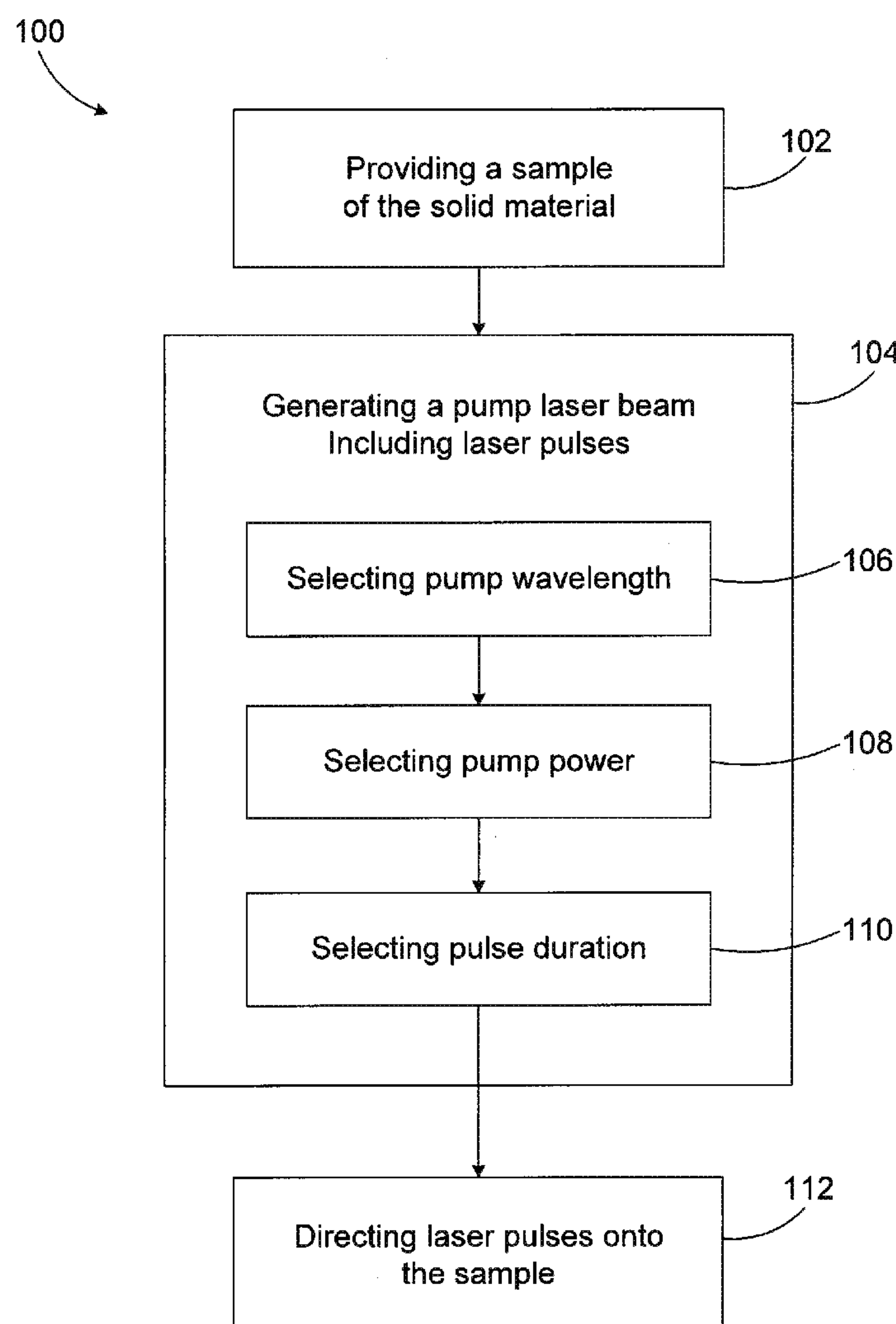


US 20120312028A1

(19) **United States**(12) **Patent Application Publication**
KASHYAP et al.(10) **Pub. No.: US 2012/0312028 A1**(43) **Pub. Date: Dec. 13, 2012**(54) **METHODS FOR LASER COOLING OF
FLUORESCENT MATERIALS**(52) **U.S. Cl. 62/3.1**(75) **Inventors:** **Raman KASHYAP**, Baie D'Urfe
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MONTREAL**, Montreal (CA)(21) **Appl. No.: 13/469,635**(22) **Filed: May 11, 2012****Related U.S. Application Data**(60) Provisional application No. 61/484,784, filed on May
11, 2011.**Publication Classification**(51) **Int. Cl.**
F25B 21/00 (2006.01)

Methods for cooling fluorescent material are provided. A first method includes providing a sample of the material having an elongated direction of light propagation, exhibiting fluorescence at a mean fluorescence wavelength and capable of emitting superradiant pulses with a formation delay time. The method then involves generating a pump pulsed laser beam having a wavelength longer than the mean fluorescence wavelength, a pump power at which superradiant pulses are emitted and a pulse duration shorter than the formation delay time. The pulses are directed onto the sample along the direction of light propagation to produce the superradiant pulses in an anti-Stokes process inducing a cooling of the sample. A second laser cooling method includes a combination of a traditional anti-Stokes cooling cycle and an upconversion cooling cycle, wherein the two cooling cycles act cooperatively to cool the sample.



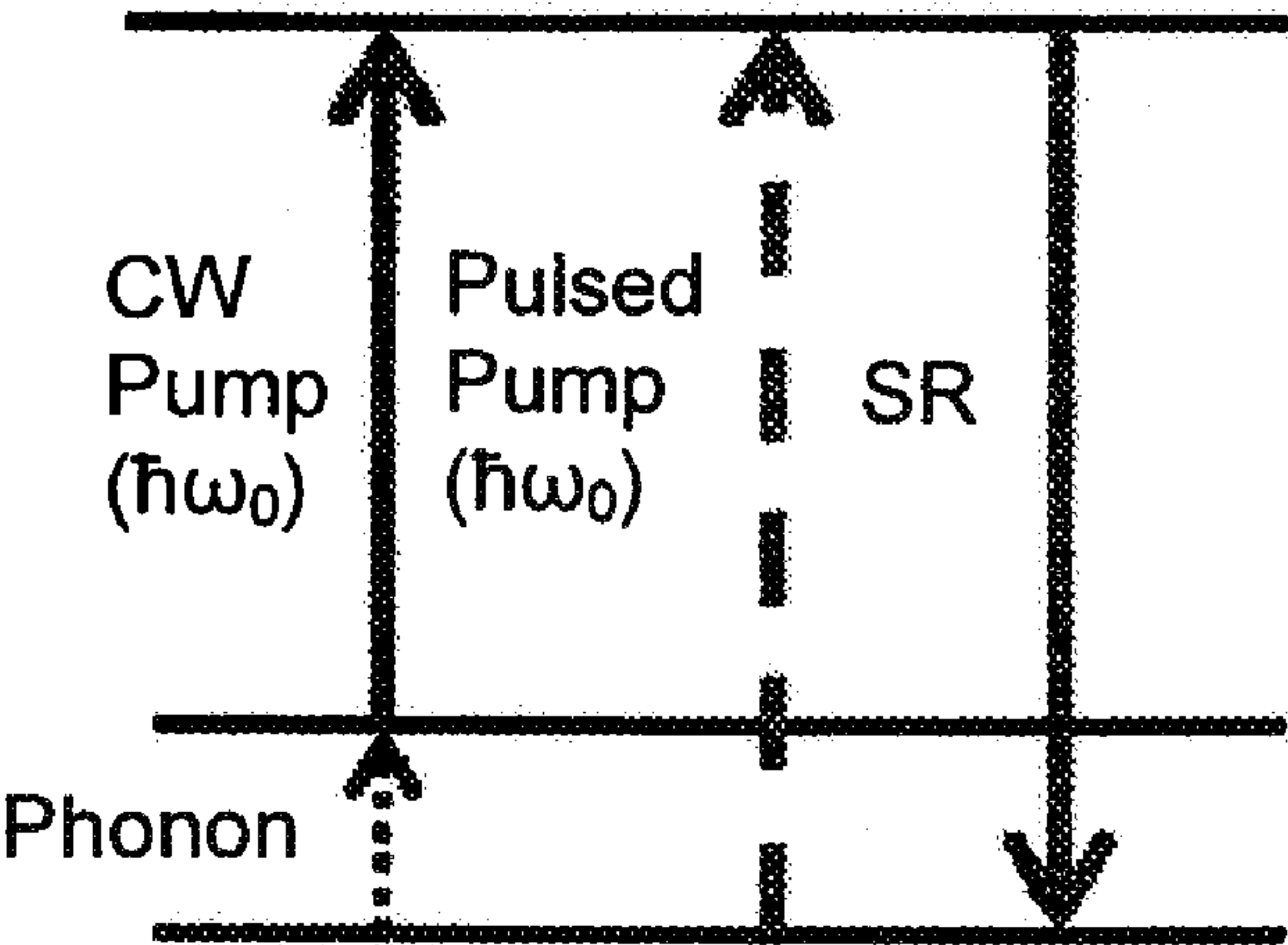


FIG. 1
(PRIOR ART)

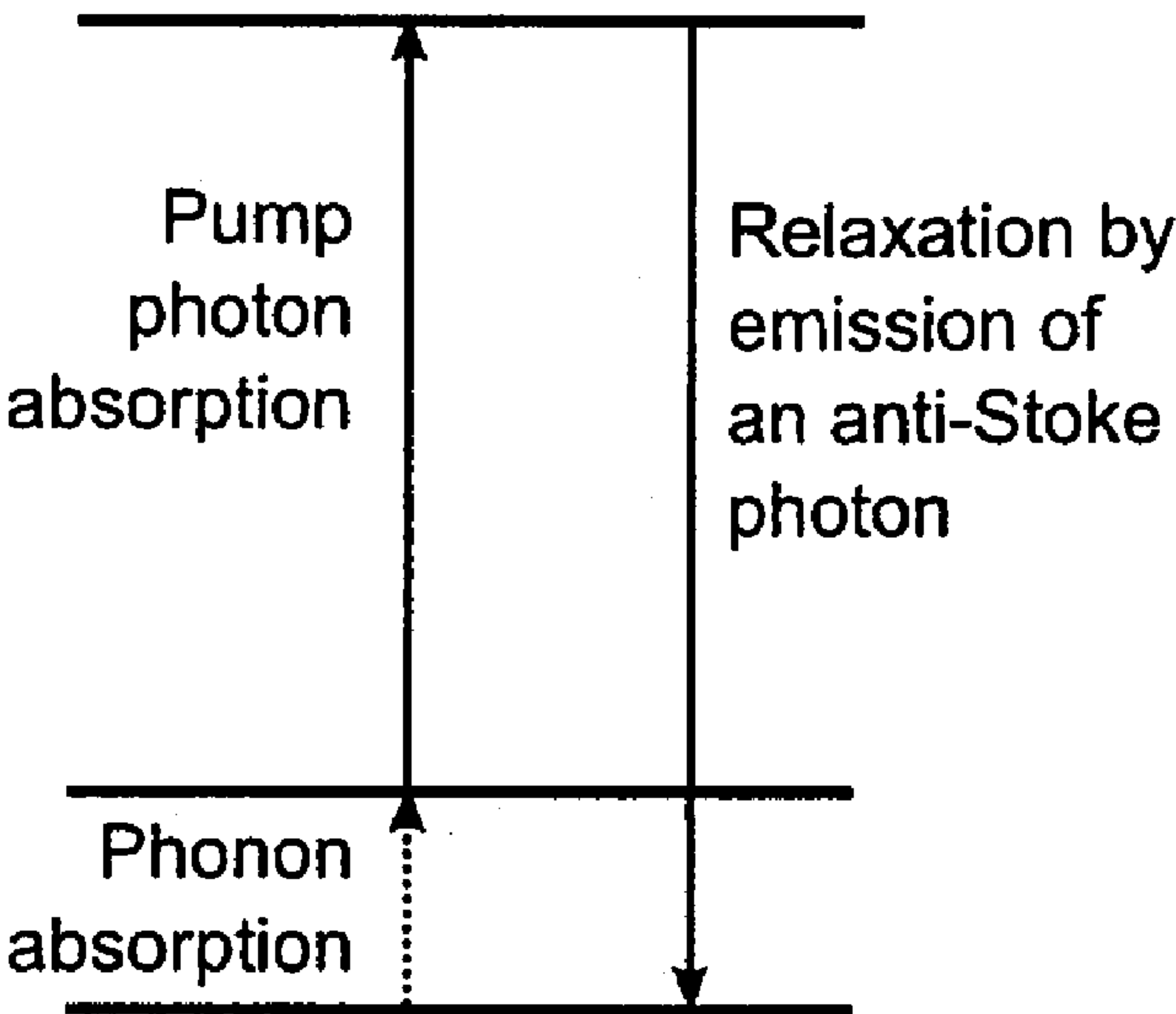


FIG. 2
(PRIOR ART)

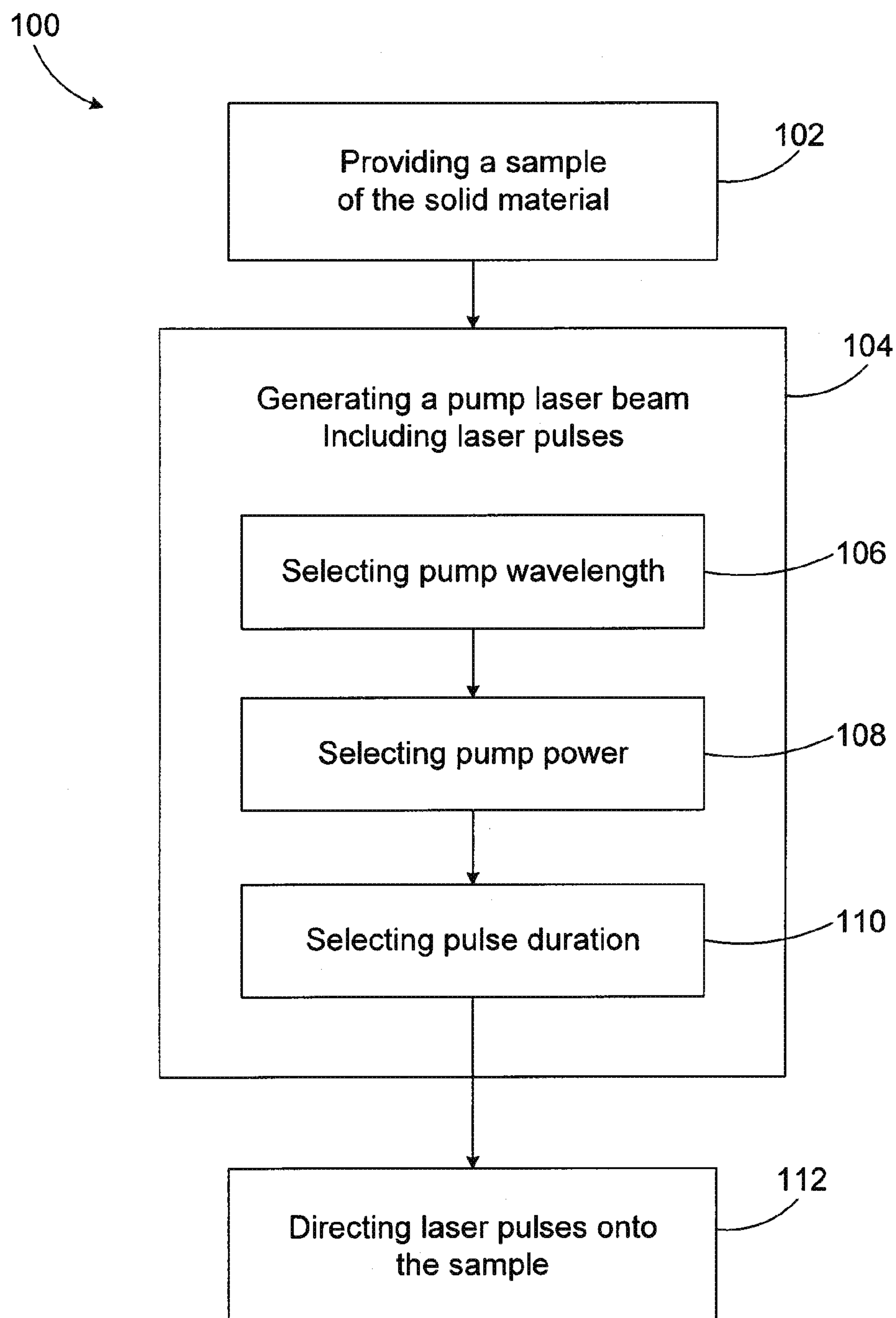


FIG. 3

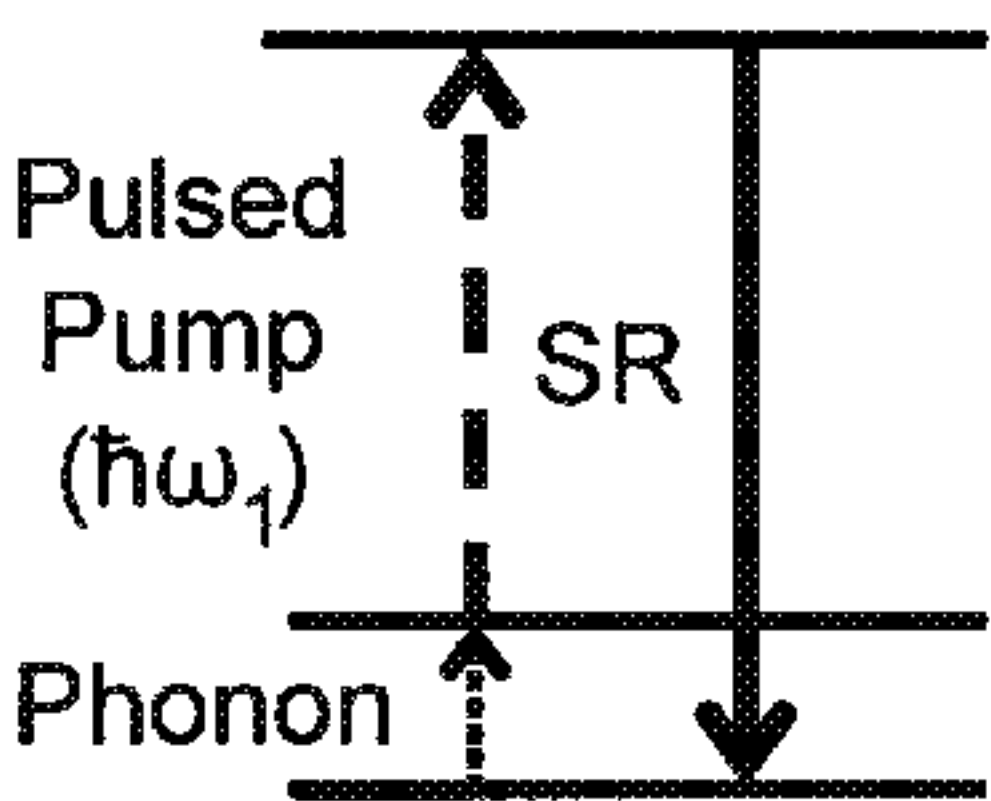


FIG. 4

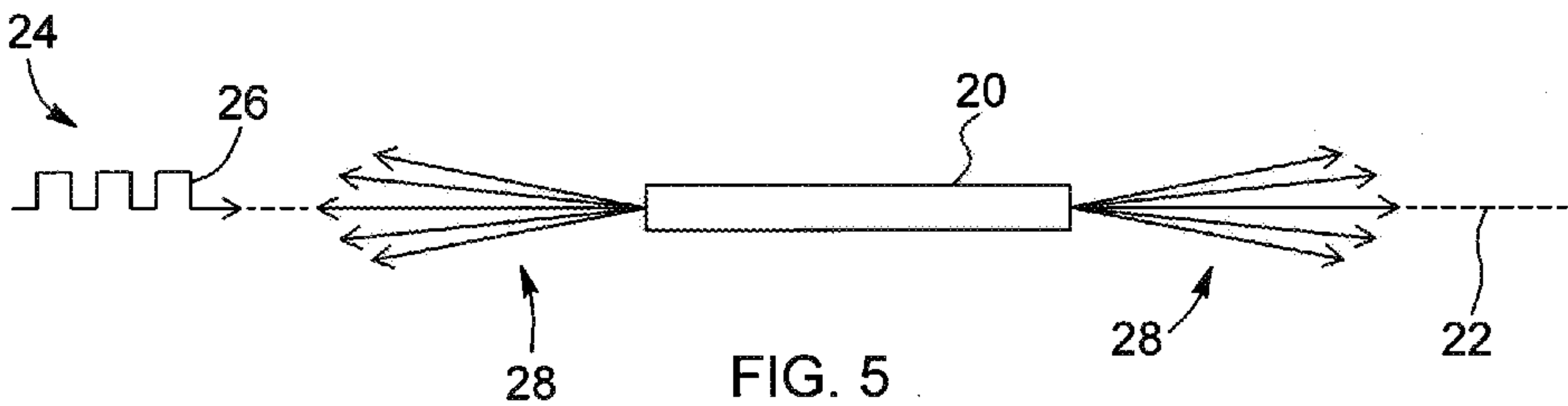


FIG. 5

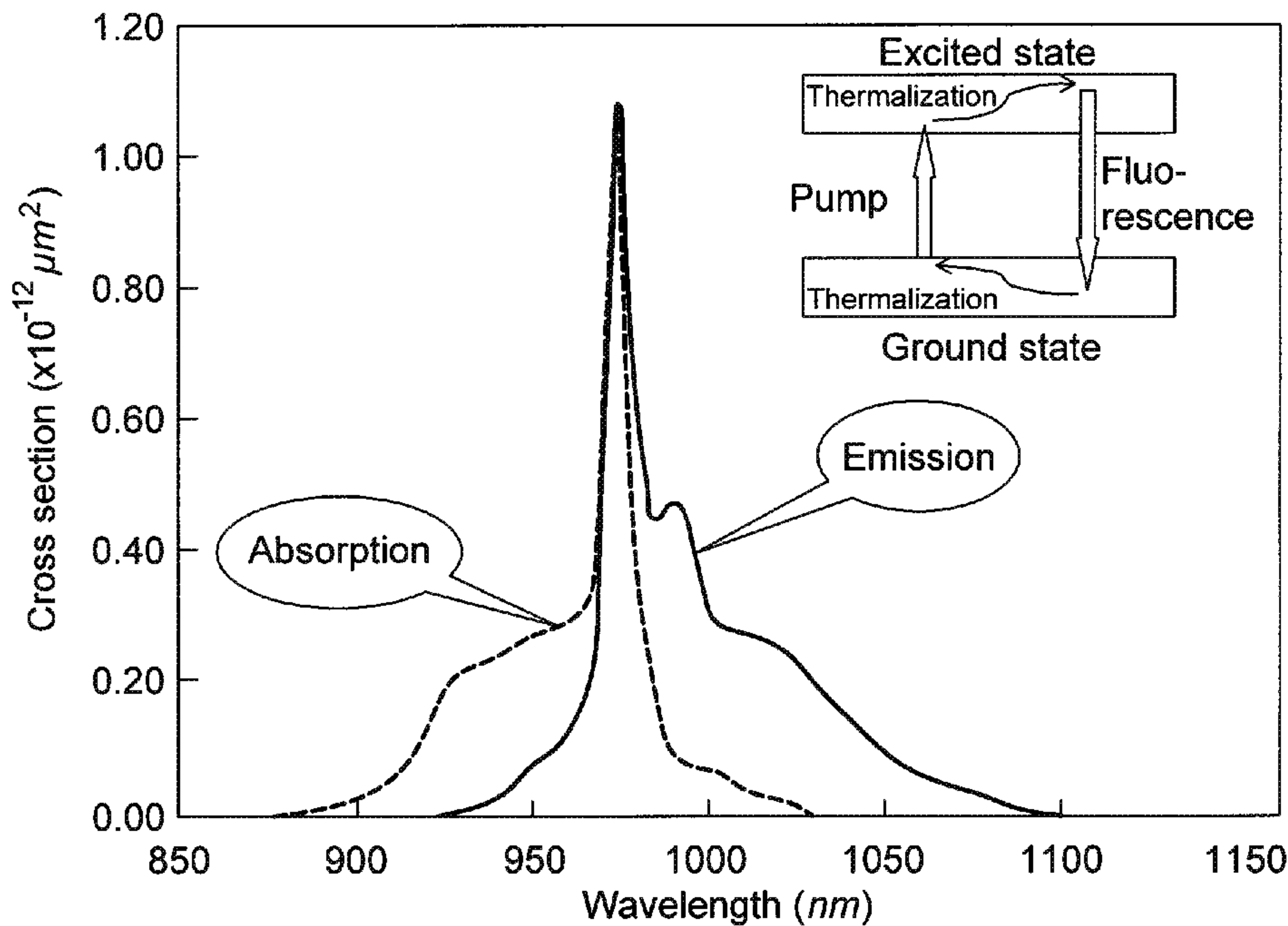


FIG. 6 (PRIOR ART)

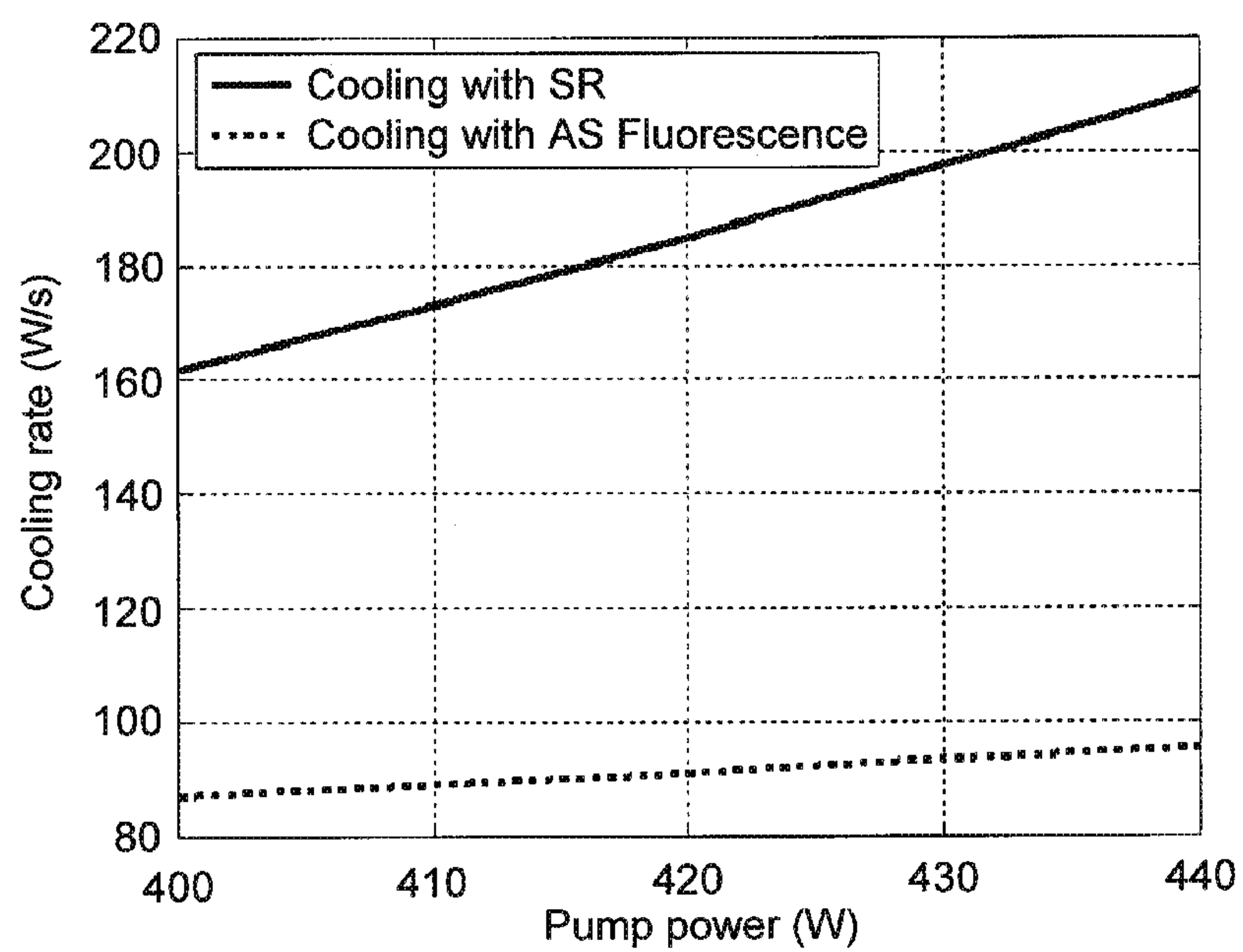


FIG. 7

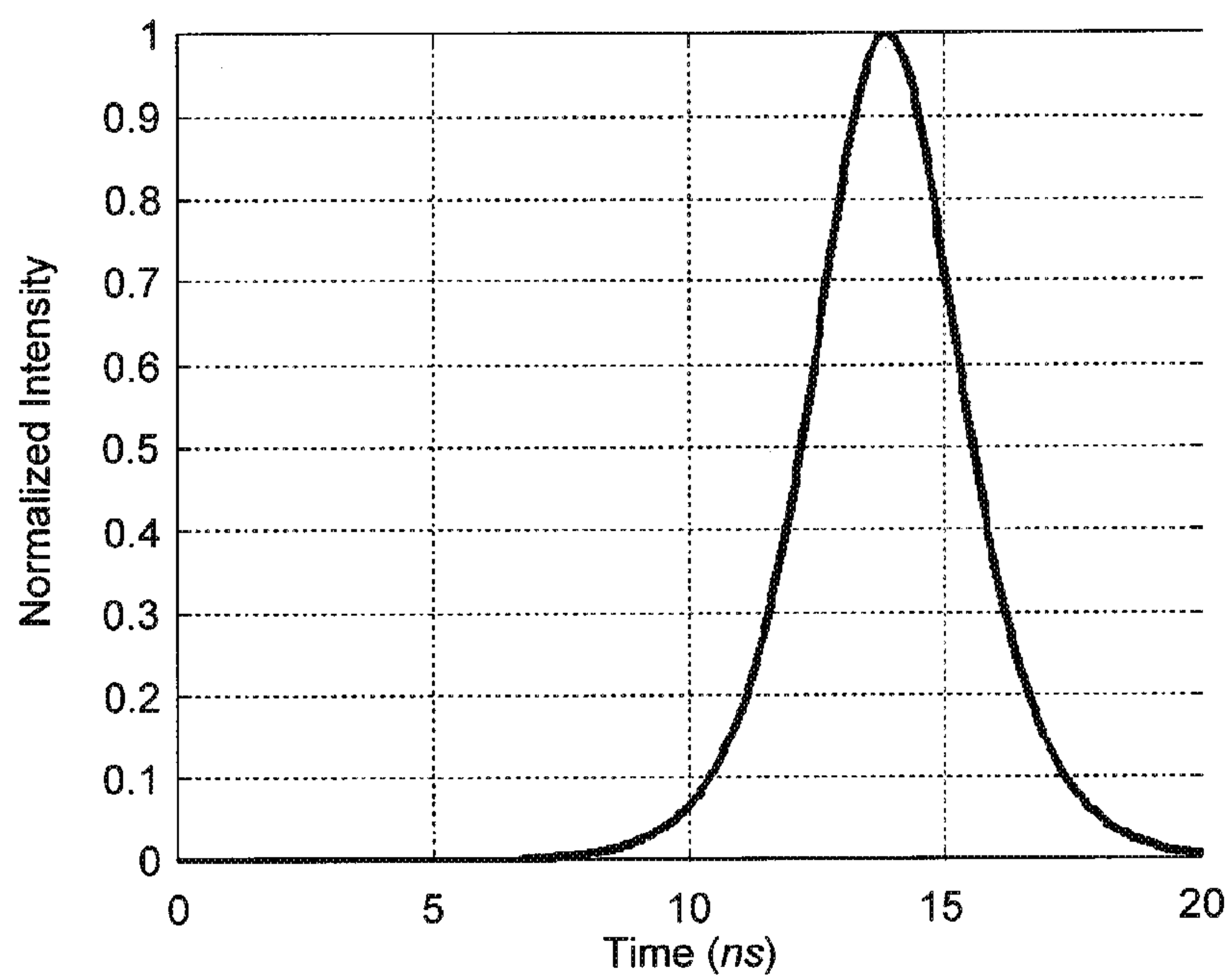


FIG. 8

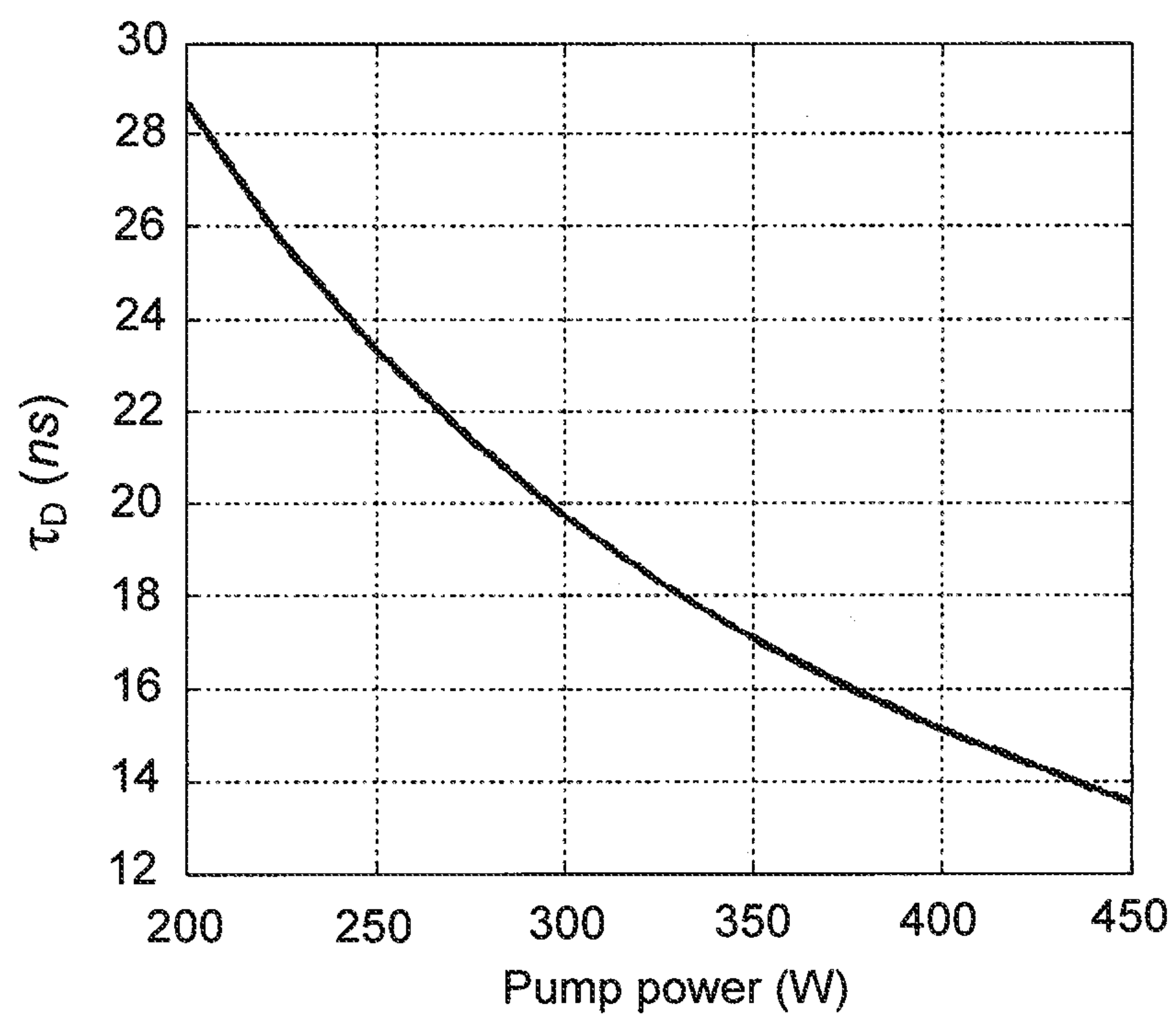


FIG. 9

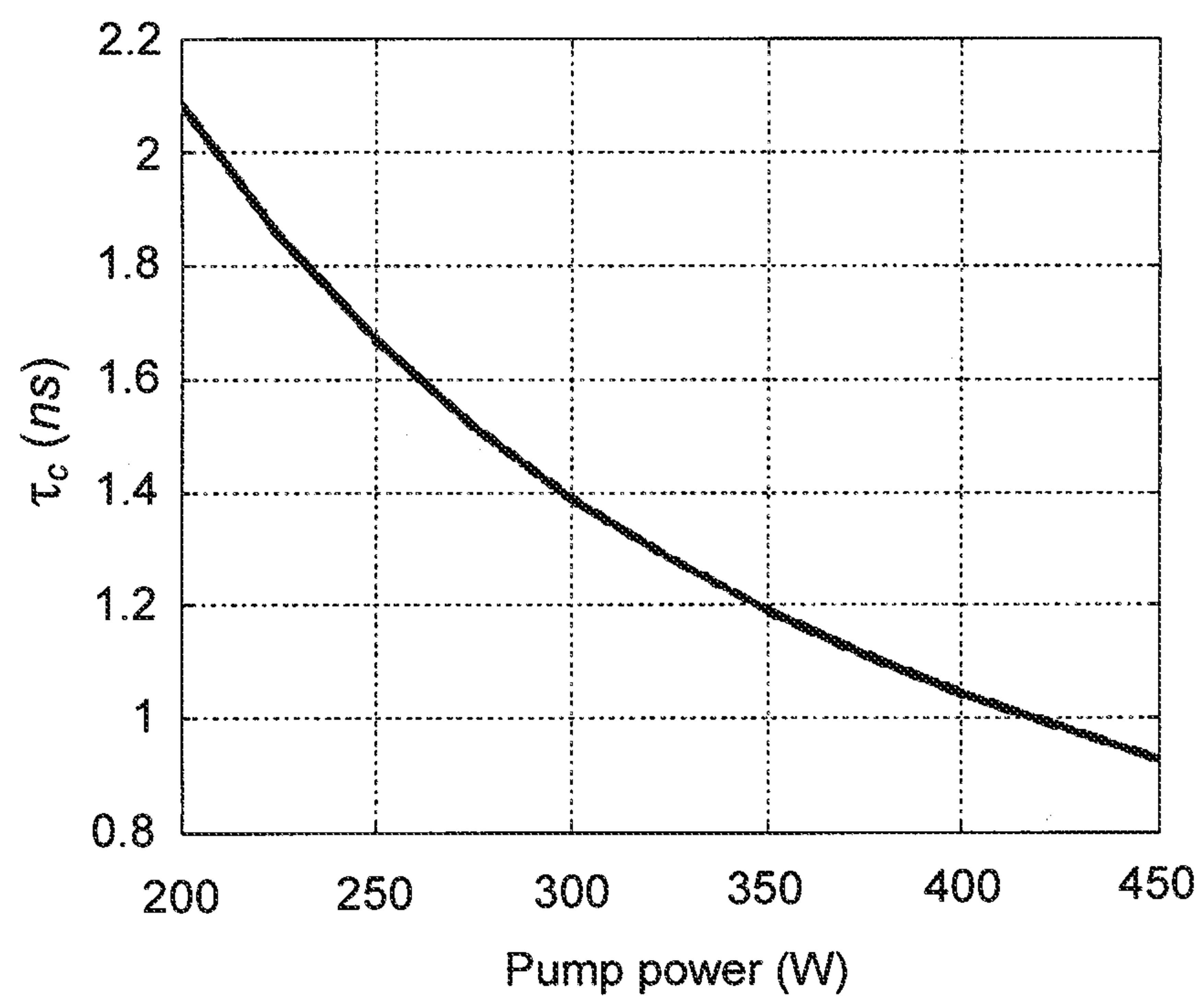


FIG. 10

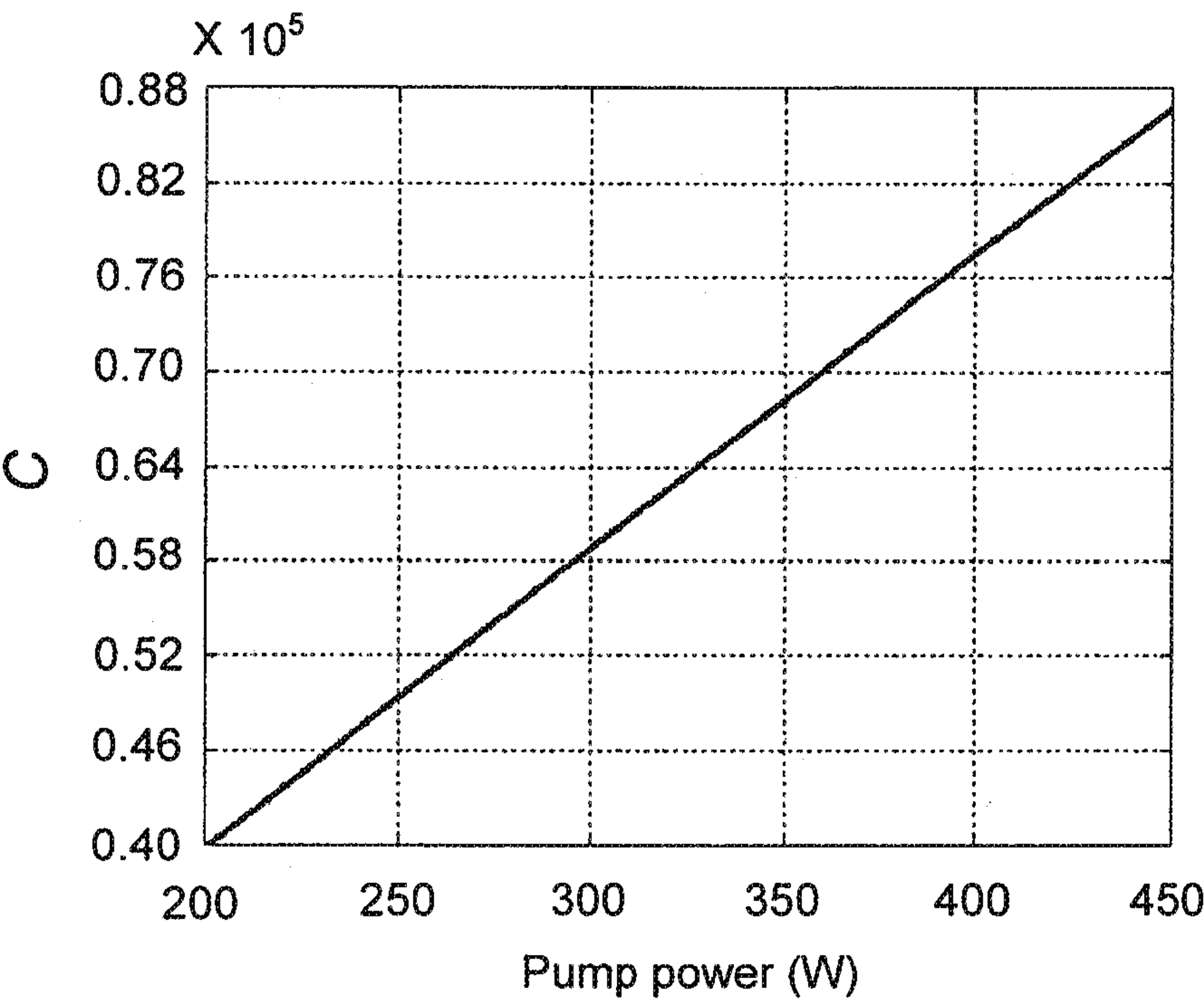


FIG. 11

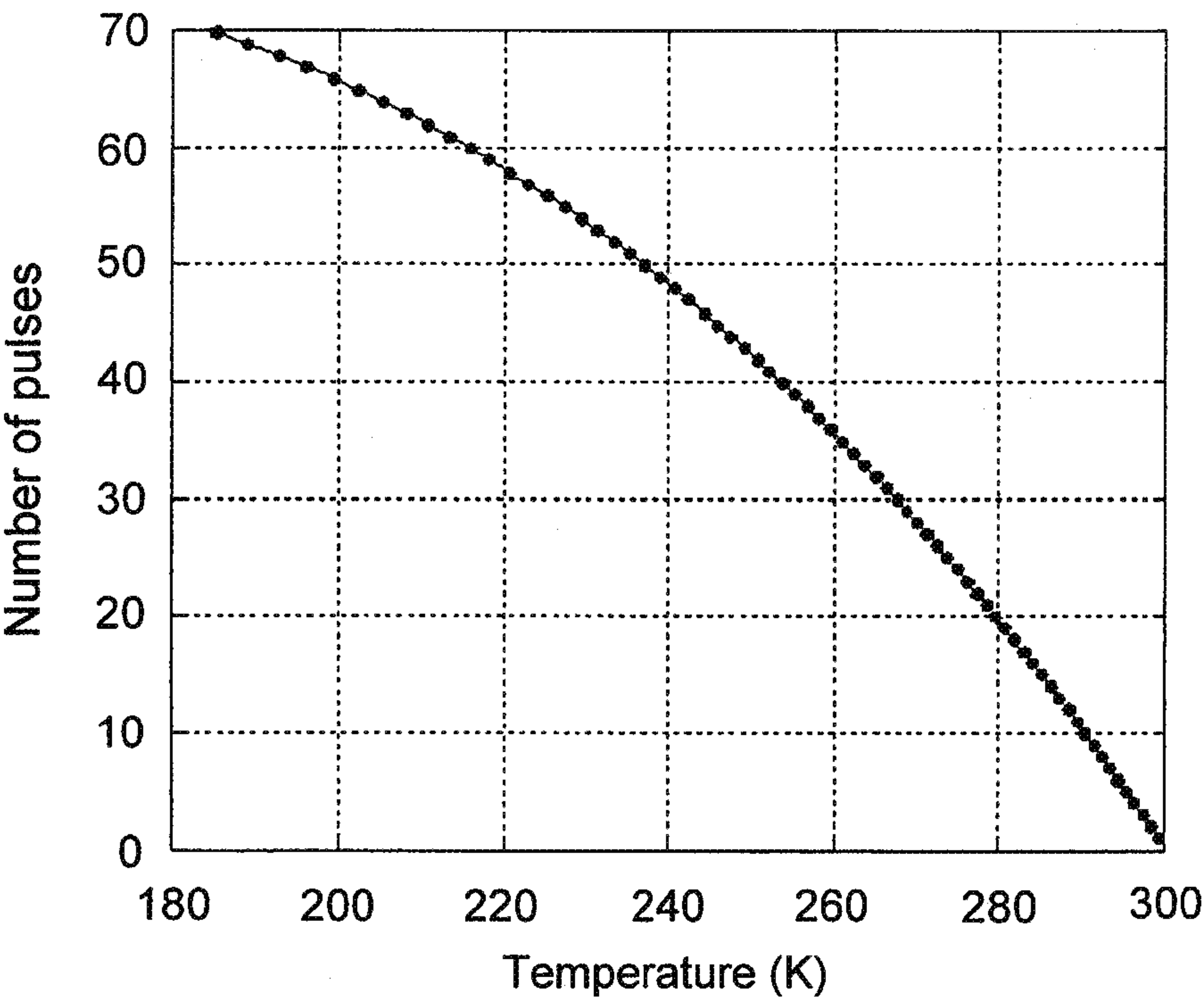


FIG. 12

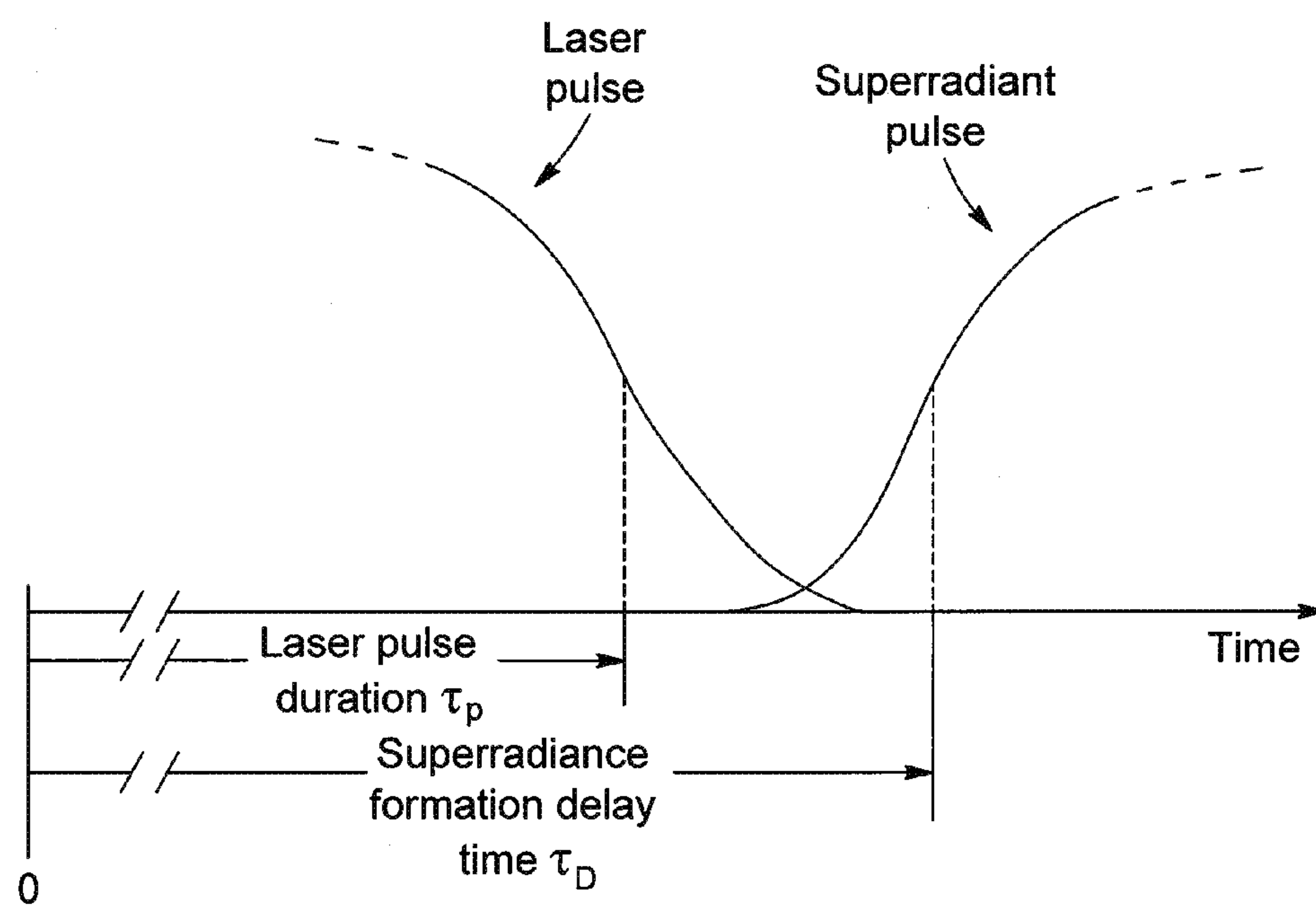


FIG. 13

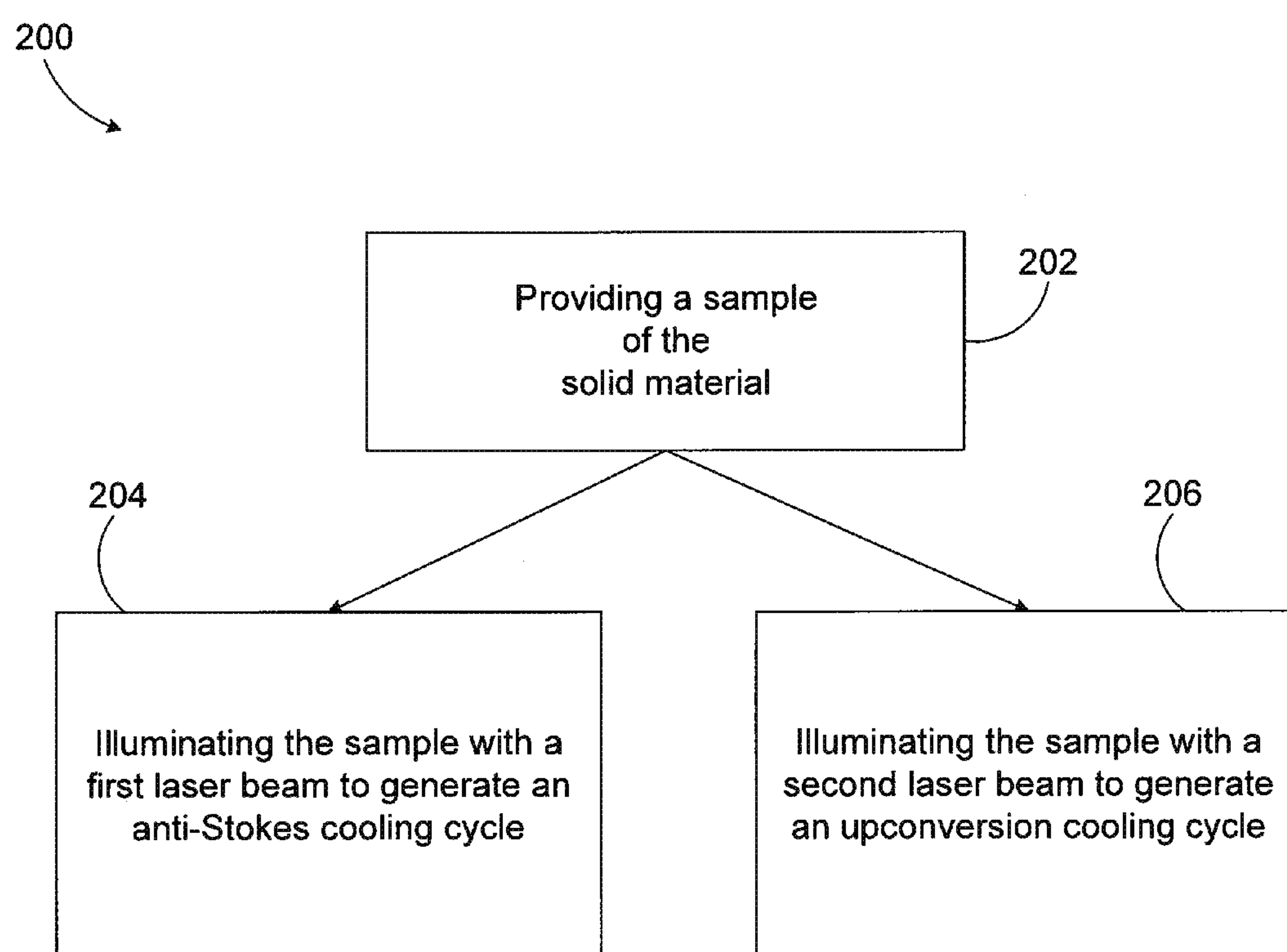


FIG. 14

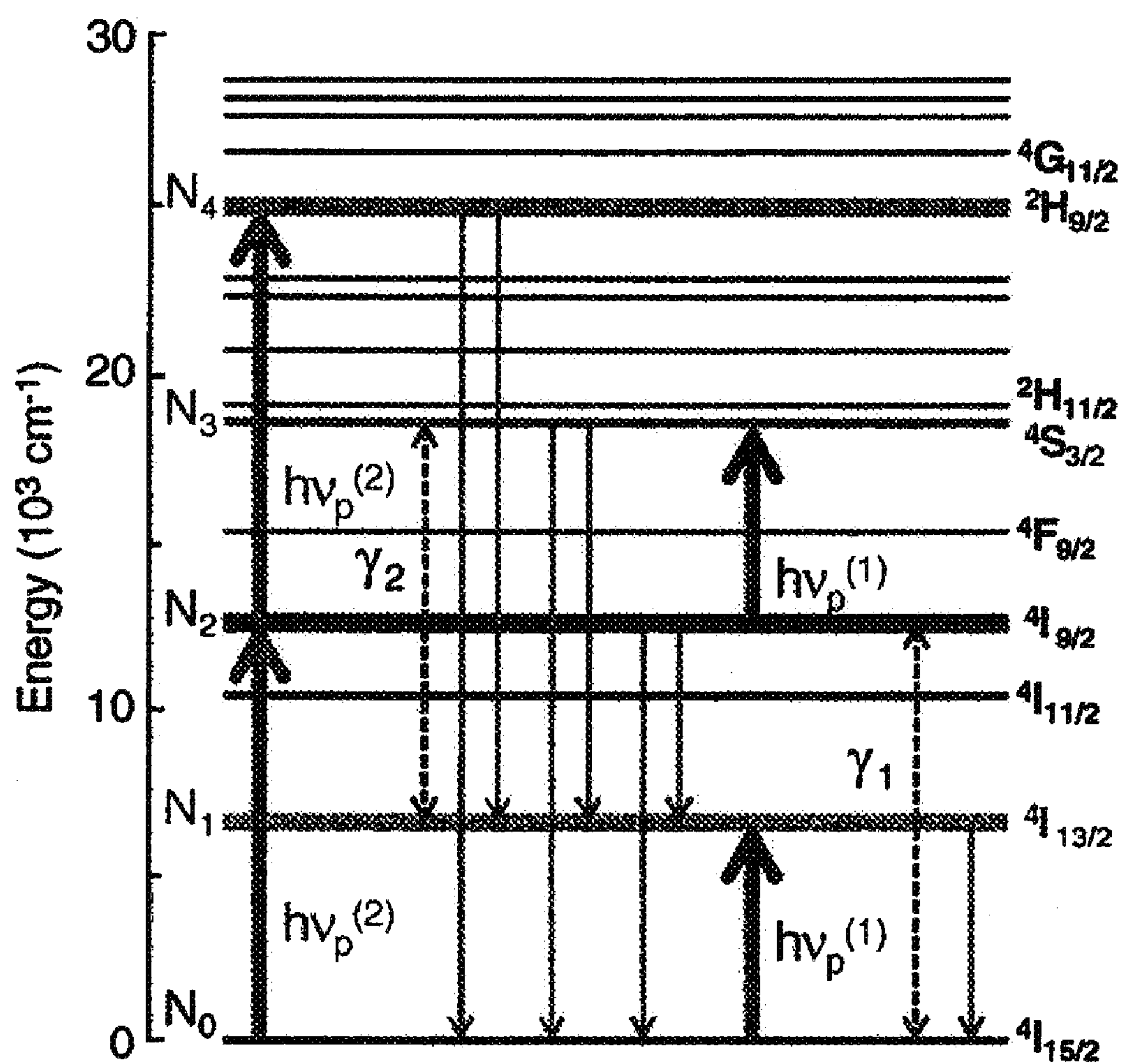


FIG. 15

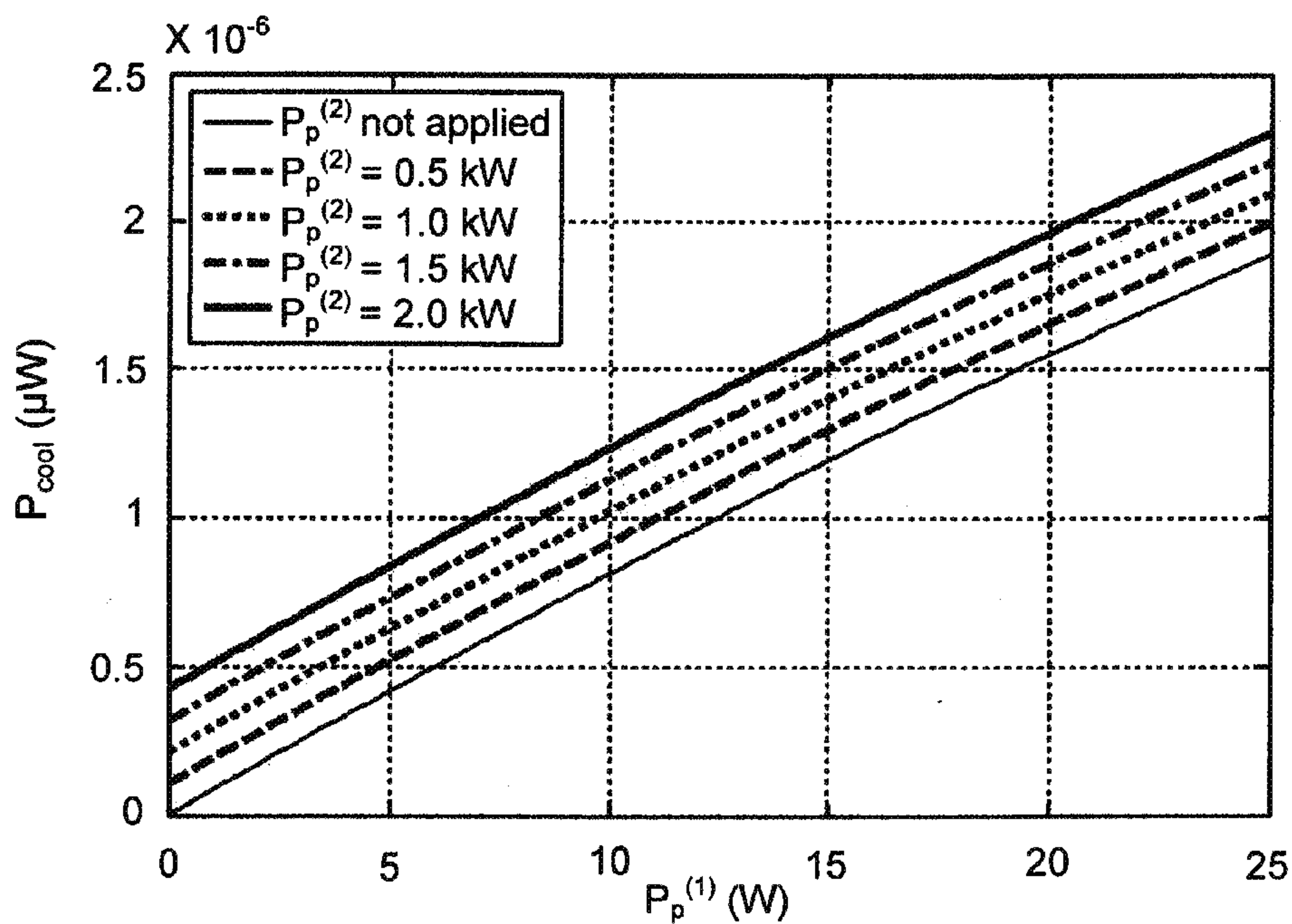


FIG. 16

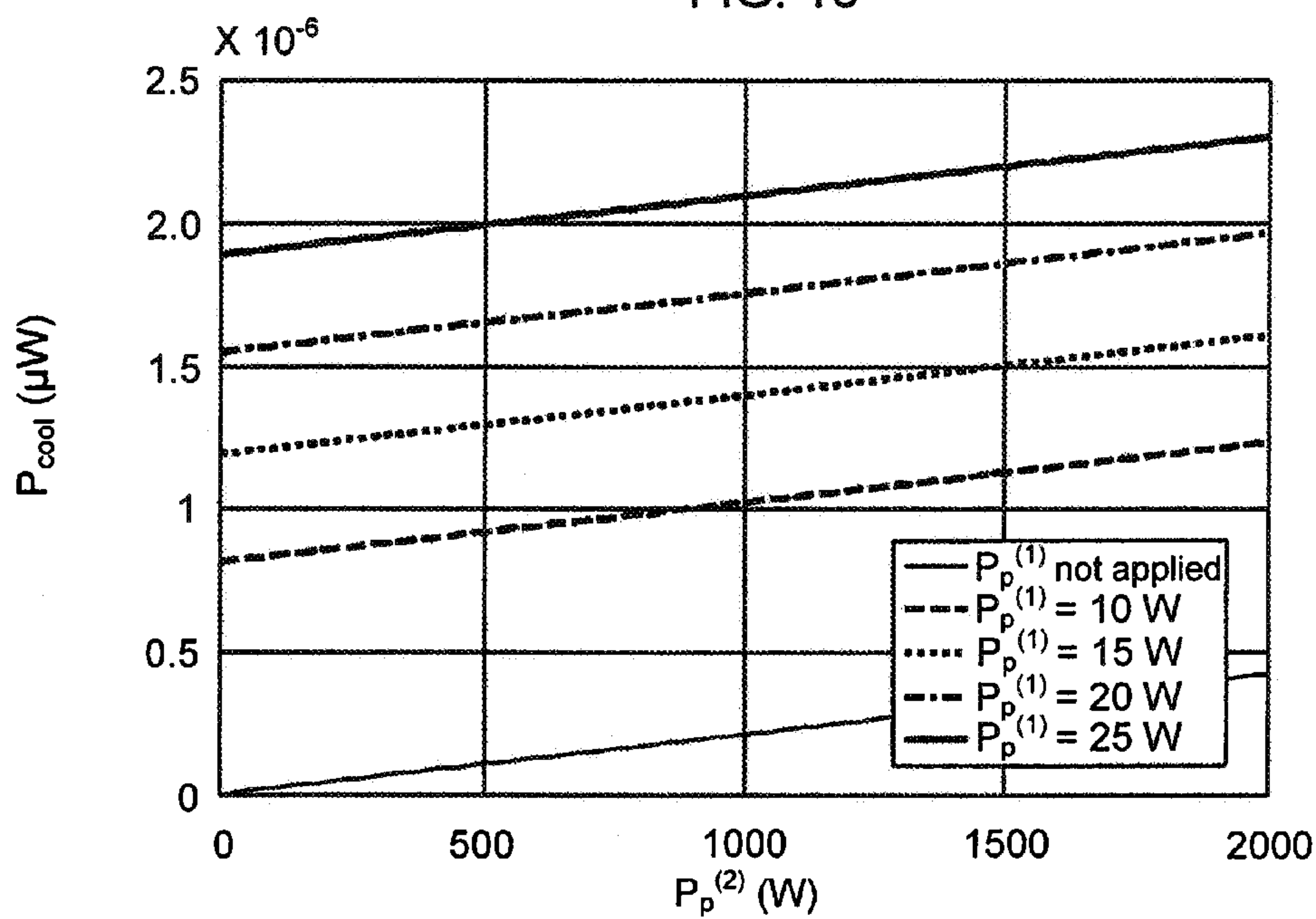


FIG. 17

METHODS FOR LASER COOLING OF FLUORESCENT MATERIALS

FIELD OF THE INVENTION

[0001] The present invention relates to the field of light-matter interaction, and more particularly concerns laser cooling methods.

BACKGROUND OF THE INVENTION

[0002] Laser cooling of solids, also referred to as optical refrigeration, optical cooling or anti-Stokes fluorescence cooling, is a fast-developing area in the field of optical science and laser physics. Apart from being of fundamental scientific interest, this topic addresses the relevant technological problem of designing and constructing laser-pumped optical coolers.

[0003] The idea of cooling solids by anti-Stokes fluorescence was proposed by Peter Pringsheim in 1929 [see P. Pringsheim, *Z. Phys.* vol. 57, p. 739, (1929)]. It has been shown that in some materials, excited atoms emit light having wavelength shorter than that of the light illuminating the material, and that the excess energy is supplemented via thermal (phonon) interactions with the excited atoms [see R. W. Wood, *Phil. Mag.* Vol. 6, p. 310, 1928]. This process was named anti-Stokes fluorescence, in contrast to the process of Stokes fluorescence in which the wavelength of the emitted photons is larger than the wavelength of the absorbed ones.

[0004] Since anti-Stokes fluorescence involves the emission of photons having energy larger than the energy of the photons that are absorbed, it may cause the removal of thermal energy (i.e. phonons) from the illuminated material and, as a result, lead to its refrigeration. Hence, anti-Stokes fluorescence has the potential to provide a basis for obtaining entirely solid-state optical coolers with the added benefits of being compact and free of mechanical vibrations, moving parts or fluids. Furthermore, such optical coolers offer several anticipated advantages over thermoelectric and mechanical coolers.

[0005] For example, optical refrigerators share the benefit of low mechanical vibrations with thermoelectric coolers based on the Peltier effect, but do not require physical contact with a heat sink in order to expel heat from the material to be cooled. Additionally, although thermoelectric coolers may be more effective than anti-Stokes optical coolers at temperatures above 190 K, the minimum cold side of thermoelectric coolers is limited to about 180 K whereas anti-Stokes optical coolers may cool materials at temperatures as low as about 90 K [see R. Frey et al. *J. Appl. Phys.* vol. 87, p. 4489 (2000)]. Furthermore, while mechanical coolers such as the Stirling cycle cooler can reach temperatures of the order 10 K, they remain large, expensive, and cause vibrations that may not be suitable in many applications. In comparison, anti-Stokes optical coolers can be based on reliable laser diode systems disposed is remote from the cooler, thereby generating low electromagnetic interference in the cooling area.

[0006] An observation of net radiation cooling of a solid by anti-Stokes fluorescence was reported in 1995 with an ytterbium-doped fluorozirconate $\text{ZrF}_4\text{—BaF}_2\text{—LaF}_3\text{—AlF}_3\text{—NaF—PbF}_2$ (ZBLANP) glass [see R. I. Epstein et al., *Nature* vol. 377, p. 500 (1995)]. In this experiment a Yb^{3+} -doped sample of ZBLANP having the shape of a rectangular parallelepiped of volume 43 mm^3 was laser-pumped at a wavelength of 1015 nm and cooled to 0.3 K below room tempera-

ture via anti-Stokes fluorescence cooling. Since this experimental demonstration, laser-induced cooling of solids has been observed in a range of glasses and crystals doped with the rare-earth ions ytterbium (Yb^{3+}), thulium (Tm^{3+}) and erbium (Er^{3+}) [see M. P. Hehlen, *Proc. SPIE* vol. 7228, p. 72280E (2009) and references therein].

[0007] Cryogenic operation in an all-solid-state refrigerator was reported in 2010 by the research group of Mansoor Sheik-Bahae from the University of New Mexico [see D. V. Seletskiy et al. *Nature Photon.* vol. 4, p. 161 (2010)]. In this study, a laser cooling of an ytterbium-doped LiYF_4 from ambient temperature to a temperature of about 155 K with a cooling power of 90 mW was demonstrated, thereby establishing a new milestone in the field of optical refrigeration. In particular, this temperature constitutes a considerable improvement in comparison with the temperatures reached with glasses and crystals doped with Tm^{3+} and Er^{3+} ions.

[0008] It should be noted that in all the experiments mentioned above, fluorescence (i.e. incoherent radiation), is involved in the cooling process. Furthermore, all excited ions in the doped host materials radiate independently from and without interacting with each other.

[0009] In this regard, in 1954, when lasers had not yet been invented, R. H. Dicke theoretically predicted a phenomenon of collective spontaneous emission of coherent radiation by an ensemble of excited particles coupled by radiation and noise field [see R. H. Dicke, *Phys. Rev.* vol. 93, p. 99 (1954)]. This collective emission was named superradiance (SR).

[0010] The experimental history of superradiance began in 1973, when it was observed in a gas of hydrogen fluoride (HF) [see N. Skribanovitz et al. *Phys. Rev. Lett.* vol. 30, p. 309 (1973)]. Experiments on superradiance in solids were carried out in the early 1980s, using O_2^- centers in KCl crystals [see R. Florian et al. *Solid State Commun.* vol. 42, p. 55 (1982); R. Florian et al., *Phys. Rev. A* vol. 28, p. 2709 (1984)] and impurity pyrene molecules in di-phenyl crystals [see P. V. Zinov'ev et al. *Sov. Phys. JETP* vol. 58, p. 1129 (1983); *Zh. Eksp. Teor. Fiz.* vol. 85, p. 1945 (1983), in Russian]. In 1999, Zuikov and colleagues reported the experimental observation of superradiant pulses in a crystal doped with rare-earth ions ($\text{Pr}^{3+}:\text{LaF}_3$) [see V. A. Zuikov et al. *Laser Phys.* vol. 9, p. 951 (1999)]. This study was a proof-of-principle experiment, which simply aimed to achieve superradiance in a rare-earth-doped crystal without any intention of cooling it.

[0011] More recently, it has been proposed and theoretically demonstrated that superradiance may be employed to intensify laser cooling of solids in the anti-Stokes regime [see S. V. Petrushkin and V. V. Samartsev, *Laser Phys.* vol. 11, p. 948 (2001); E. K. Bashkurov, *Phys. Lett. A* vol. 341, p. 345 (2005); S. N. Andrianov and V. V. Samartsev, *Laser Phys.* vol. 7, p. 314 (1997)]. In these studies, two-level impurity ions with resonance frequency ω_0 were pumped with two optical pump fields: a continuous-wave (CW) laser field with frequency $\omega_1 < \omega_0$, and a pulsed laser field with frequency ω_0 . As can be seen from FIG. 1 (PRIOR ART), only the CW pump laser, with a $\omega_1 < \omega_0$, contributes in exciting the two-level ions with simultaneous absorption of phonons from the host material and thus in cooling the system. On the other hand, since its frequency coincides with the resonance frequency of the two-level ion system, the pulsed laser is not involved in the cooling process, but merely promotes ions from the ground state to the excited state of the two-level system without absorption of phonons.

[0012] In the configuration shown in FIG. 1 (PRIOR ART), the pulsed laser thus serves as a catalyst in triggering the onset of the superradiance regime by accelerating the radiative relaxation rate of the ions. Indeed, the ions excited by the pulsed laser (i.e. without absorption of phonons) become correlated with the ions excited by the CW laser (i.e. with absorption of phonons), which results in an ensemble of correlated excited ions that relaxes to the ground state at an accelerated radiative rate in a superradiant fashion. However, in the process, the pulsed laser may generate phonons, which heat the system and therefore counteract the cooling effect provided by the CW laser. It will thus be understood that optical cooling of the material should involve a net decrease in the phonon population, that is, that the number of absorbed phonons per unit time should exceed that of emitted phonons.

[0013] Recently, an alternative cooling cycle based on the phenomenon of upconversion was proposed and theoretically described [see A. J. Garcia-Adeva et al., Phys. Rev. B, vol. 79, p. 033110 (2009)]. More particularly, the alternative cooling cycle considered therein exploits the efficient infrared-to-visible upconversion process that is often found in rare-earth-doped low-phonon-energy host materials characterized by reduced multiphonon transition rates. In this case, the pump level acts as an intermediate photon reservoir from which excited-state absorption takes place.

[0014] Potassium-lead chloride crystal (KPb_2Cl_5) was synthesized in 1993 [see K. Nitsch et al., J. Cryst. Growth vol. 131, p. 612 (1993)]. It possesses high chemical resistance, satisfactory mechanical properties, and is only slightly hygroscopic. Moreover, due to its low-energy phonon spectrum (maximum phonon energy of about 203 cm^{-1}) and associated low non-radiative relaxation rates, KPb_2Cl_5 crystal emerges as an interesting candidate for optical cooling applications. In this regard, samples of erbium-doped potassium-lead chloride ($\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$) have been cooled following either a traditional anti-Stokes cooling cycle [see N.J. Condon et al., Opt. Express vol. 17, p. 5466 (2009)] or an upconversion-based cooling cycle [see J. Fernandez et al., Phys Rev. Lett. vol. 97, p. 033001 (2006)].

[0015] In the first case, a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ was cooled via a traditional cooling cycle involving the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition pumped at wavelengths longer than 1557 nm, that is, 17 nm longer than the mean fluorescence wavelength of 1540 nm. As a result of the refrigeration process, the sample was cooled by only 0.01 K below ambient temperature. In the second case, an $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ sample was cooled with infrared-to-visible upconversion involving the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$ transitions at pump wavelengths exceeding the mean fluorescence wavelength of 852.5 nm, wherein the $^4\text{I}_{9/2}$ level acts as an intermediate electron reservoir from which the excited state absorption process takes place. In this experiment the temperature of the sample dropped by 0.7 ± 0.1 K. Hence, it should be emphasized that the cooling efficiency was very low for both the traditional and the upconversion-based cooling cycles.

[0016] In view of the above considerations, there exists a need for more efficient methods for laser cooling of materials, which alleviate at least some of the drawbacks of the prior art.

SUMMARY OF THE INVENTION

[0017] According to a first aspect of the invention, there is provided a method for cooling a fluorescent material. The method includes the steps of:

[0018] a) providing a sample of the fluorescent material, the sample having an elongated light propagation direction, the fluorescent material exhibiting fluorescence at a mean fluorescence wavelength and being capable of entering a superradiance regime wherein superradiant pulses are emitted with a formation delay time;

[0019] b) generating a pump laser beam including laser pulses. The generating includes the substeps of:

[0020] i) selecting a pump wavelength of the pump laser beam that is longer than the mean fluorescence wavelength of the fluorescent material;

[0021] ii) selecting a pump power of the pump laser beam so as to reach the superradiance regime of the fluorescent material; and

[0022] iii) selecting a pulse duration of the laser pulses that is shorter than the formation delay time of the superradiant pulses; and

[0023] c) directing the laser pulses of the pump laser beam onto the sample of the fluorescent material along the elongated light propagation direction thereof so as to produce the superradiant pulses in an anti-Stokes process inducing a cooling of the sample.

[0024] In some embodiments, the fluorescent material is a solid material including a host material doped with ions of a rare-earth element.

[0025] Advantageously, the above laser cooling method provides, due in part to the high radiative relaxation rate of the superradiant pulses, an improved anti-Stokes cooling cycle that is more efficient and capable of reaching lower temperatures than traditional cooling cycles based on incoherent anti-Stokes fluorescence.

[0026] Moreover, in embodiments wherein the fluorescent material is a rare-earth-doped host material, the laser cooling method relaxes the constraints on the use of low-phonon-energy materials as host materials by allowing the use of materials having higher phonon energy, which have been thus far considered unsuitable as rare-earth-doped hosts for traditional laser cooling applications.

[0027] Further advantageously, contrary to previous known methods employing superradiance to intensify laser cooling of solids in the anti-Stokes regime, the laser cooling method above may be realized by using a single pulsed pump laser beam at a pump wavelength longer than a mean fluorescence wavelength of the solid material to be cooled. Indeed, in methods known in the art, both a CW and a pulsed pump laser sources are employed, whereby the latter generate phonons that heat the material, thus reducing the efficiency of the cooling cycle. The above method helps circumventing this problem.

[0028] According to another aspect of the invention, there is provided a method for cooling a fluorescent material. The method includes the steps of:

[0029] a) providing a sample of the fluorescent material, the fluorescent material having an absorption spectrum including at least one absorption band, each of the at least one absorption band having a corresponding maximum absorption wavelength;

[0030] b) illuminating the sample of the fluorescent material with a first pump laser beam having a first pump wavelength that is longer than the corresponding maximum absorption wavelength of one of the at least one absorption band, so as to generate an anti-Stokes cooling cycle; and, simultaneously,

[0031] c) illuminating the sample of the fluorescent material with a second pump laser beam having a second pump wavelength, the second pump wavelength being selected for exciting electrons of the fluorescent material so as to generate an upconversion cooling cycle, wherein the anti-Stokes and the upconversion cooling cycles act cooperatively to induce a cooling of the sample of the fluorescent material.

[0032] In some embodiments, the fluorescent material is a solid material including a host material doped with ions of a rare-earth element.

[0033] Advantageously, by combining a traditional anti-Stokes cooling cycle and an upconversion cooling cycle, the method according to this aspect of the invention helps overcoming the self-termination effects that may be present in either of the two cooling cycles when used on its own.

[0034] Other features and advantages of the present invention will be better understood upon reading of preferred embodiments thereof with reference to the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] FIG. 1 (PRIOR ART) illustrates a laser cooling method with superradiance that employs both a continuous-wave laser pump and a pulsed laser pump to generate cooling.

[0036] FIG. 2 (PRIOR ART) is a schematic energy diagram illustrating a process of laser cooling according to which the absorption of a pump photon by the material is followed by rapid thermalization within the excited state with the absorption of phonons and subsequent emission of anti-Stokes fluorescence.

[0037] FIG. 3 is a flow chart of a method for laser cooling of a fluorescent material according to an embodiment of the invention.

[0038] FIG. 4 is a schematic energy diagram of a laser cooling method with superradiance according to an embodiment of the invention.

[0039] FIG. 5 is a schematic representation of a sample of a ZBLAN host material doped with Yb^{3+} illuminated by the laser pulses of a pump laser beam and emitting superradiant pulses, according to an embodiment of the invention.

[0040] FIG. 6 (PRIOR ART) shows the spectra of absorption and emission cross-sections of Yb^{3+} ions in a ZBLAN host material at room temperature. The inset schematic energy diagram illustrating anti-Stokes cooling.

[0041] FIG. 7 is graph comparing the cooling rate as a function of the pump power P_p provided by a laser cooling method according to an embodiment of the invention (solid line) and by a traditional anti-Stokes cooling cycle (dotted line).

[0042] FIG. 8 is a graph showing the normalized power of a superradiant pulse as a function of time according to an embodiment of the invention.

[0043] FIG. 9 is a graph showing the formation delay time τ_D of a superradiant pulse as a function of the pump power of a pump laser beam with laser pulses having a pulse duration $\tau_p=10$ ns, according to an embodiment of the invention.

[0044] FIG. 10 is a graph showing the time of correlation self-formation τ_c of a superradiant pulse as a function of the pump power of a pump laser beam with laser pulses having a pulse duration $\tau_p=10$ ns, according to an embodiment of the invention.

[0045] FIG. 11 is a graph showing the ratio C of the power P_{SR} removed from the sample via superradiance to the power

P_{SP} removed from the sample via incoherent anti-Stokes fluorescence as a function of the pump power of a pump laser beam with laser pulses having a pulse duration $\tau_p=10$ ns, according to an embodiment of the invention.

[0046] FIG. 12 is a graph showing the number of laser pulses of the pump laser beam as a function of sample temperature, according to an embodiment of the invention.

[0047] FIG. 13 illustrates a laser pulse of pump laser beam having a pulse duration τ_p that is shorter than the formation delay time τ_D of a superradiant pulse.

[0048] FIG. 14 is a flow chart of another method for laser cooling of a fluorescent material according to an embodiment of the invention.

[0049] FIG. 15 illustrates the energy levels of the rare-earth ion Er^{3+} in a KPb_2Cl_5 host crystal.

[0050] FIG. 16 is a graph showing the net cooling power P_{cool} of a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ as a function of the pump power $P_p^{(1)}$ of the first pump laser beam, at a wavelength $\lambda_p^{(1)}=1567$ nm, for different values of the second pump power $P_p^{(2)}$ of the second pump laser beam, at a wavelength $\lambda_p^{(2)}=860$ nm, according to an embodiment of the invention.

[0051] FIG. 17 is a graph showing the net cooling power P_{cool} of a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ as a function of the pump power $P_p^{(2)}$ of the second pump laser beam, at a wavelength $\lambda_p^{(2)}=860$ nm, for different values of the first pump power $P_p^{(1)}$ of the first pump laser beam, at a wavelength $\lambda_p^{(1)}=1567$ nm, according to an embodiment of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

[0052] The present invention generally relates to methods for cooling a fluorescent material with laser radiation. As known in the art, laser cooling of materials, also referred to as optical refrigeration, optical cooling or anti-Stokes fluorescence, may occur in a fluorescent material that absorbs pumping laser radiation at one wavelength and subsequently emits fluorescent radiation that has an average wavelength shorter than that of the pumping laser radiation.

[0053] It is known in the art that an electron may be excited by a photon having an energy corresponding to a difference in energy between two atomic levels. Moreover, it is also known that phonons—quanta of vibrational energy that generates heat—may also be part of the excitation process of an electron by being absorbed thereby, along with a pump photon, in order to provide the appropriate energy for promoting the electron to an upper atomic level. Accordingly, when the excited electron relaxes in a radiative way, the emitted photon has an energy that is higher than that of the pump photon.

[0054] In laser cooling of fluorescent materials, the excess energy involved in emitting anti-Stokes photons may be provided by extracting phonons from the material. This phonon extraction via anti-Stokes emission of radiation leads to a decrease of the thermal energy stored inside the material, which may lead to optical cooling thereof if the phonon extraction rate is higher than the phonon absorption rate so that the material exhibits net anti-Stokes fluorescence. FIG. 2 (PRIOR ART) shows a schematic energy diagram illustrating a process of laser cooling according to which the absorption of a pump photon by the material is followed by rapid thermalization within the excited state with the absorption of phonons and subsequent emission of anti-Stokes fluorescence.

[0055] In this regard, it should be understood that expressions such as “traditional anti-Stokes cooling cycle” or “inco-

herent anti-Stokes fluorescence” are used herein to refer to methods that are known in the art and that are based on the cooling process illustrated in FIG. 2 (PRIOR ART). In particular, the two methods described below provide improved and more efficient laser cooling methods when compared to what is known in the art.

[0056] In the present description, the term “thermalization” is understood to refer to the absorption of phonons by electrons found on an electronic level in order to increase the energy thereof. For typical host materials involved in optical cooling applications, the thermalization process usually takes on a time scale of the order of picoseconds or less. Moreover, as used herein, the term “phonon” refers to a quasiparticle characterized by the quantization of the collective modes of vibrational energy of elastic structures of interacting particles in condensed matter. It should be noted that while phonons are typically studied in periodic materials (e.g. crystals), they may also exist in non-periodic or amorphous materials (e.g. glasses).

[0057] It will thus be understood by one skilled in the art that laser cooling requires that the wavelength of the pump photons be larger than the mean fluorescence wavelength of the anti-Stokes photons. In this context, an ideal cooling cycle of a material may be characterized by a cooling efficiency η_{cool} given by

$$\eta_{cool,ideal} = (h\nu_F - h\nu_p) / h\nu_p = (\lambda_p - \lambda_F) / \lambda_F, \quad (1)$$

which represents the fractional cooling energy provided by each absorbed pump photon. In Equation (1), $h \approx 6.63 \times 10^{-34}$ J·s, is the Planck constant, ν_p and λ_p are the frequency and wavelength of the pump photon, respectively, and ν_F and λ_F are the mean fluorescence frequency and wavelength of the anti-Stokes photons. However, if the excited electron may alternatively decay non-radiatively, for example via multiphonon emission, and thus introduce undesired heating of the material.

[0058] As known in the art, the competition between radiative and non-radiative decays may be characterized by the internal quantum efficiency

$$\eta = \frac{W_r}{W_r + W_{nr}}, \quad (2)$$

where W_r and W_{nr} are the radiative and non-radiative multiphonon relaxation rates, respectively. It will be understood that a non-zero value for W_{nr} reduces the cooling efficiency from that of the ideal cooling cycle to

$$\eta_{cool} = (\lambda_p - \lambda_F) / \lambda_F \quad (3)$$

so that the non-radiative relaxation rate of the laser-pumped excited levels should be as small as possible in comparison to the radiative relaxation rate.

[0059] The multiphonon relaxation rate may be expressed as [see H. W. Moos, J. Luminesc. vol. 1-2, p. 106 (1970)]:

$$W_{nr} = B[n(T)+1]^p \exp(-\alpha \Delta E_g), \quad (4)$$

where $n(T) = [\exp(\hbar\omega_{eff}/k_B T) - 1]^{-1}$ is the Bose-Einstein occupation number at temperature T of the effective phonon of energy $\hbar\omega_{eff}$ involved in the transition, $\hbar = h/2\pi$ is the reduced Planck constant, and $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. Moreover, B and α are material-dependent parameters that should be determined empirically. Finally, ΔE_g is

the energy gap between two phonon manifolds is that is bridged by p phonons in the multiphonon relaxation process.

[0060] It should be noted that, in most cases, the effective phonons involved in non-radiative relaxation processes are the highest-energy phonons available in the material, since this minimizes the number of phonons required to bridge a given energy gap and results in the lowest possible order for the decay process. Alternatively, in some other cases, this may not be true if the coupling strengths or density of states of lower-energy phonons are greater than those of high-energy phonons.

[0061] Furthermore, it is known in the art that in order to provide efficient optical refrigeration, via traditional anti-Stokes cooling the maximum phonon energy $\hbar\omega_{max}$ of the material and the energy $E_p = h\nu_p$ of the pump photons should fulfill the condition [see M. P. Hehlen, Proc. SPIE vol. 7228, p. 72280E (2009)]

$$E_p > 8\hbar\omega_{max}, \quad (5)$$

which indicates that more than eight phonons should be involved to bridge the energy gap corresponding to the pump photon energy E_p .

[0062] It should be mentioned that the laser cooling methods according to embodiments of the invention may generally be applied to any fluorescent material. The term “fluorescent material” as used herein is intended to refer to any substance which, in response to irradiation by electromagnetic radiation, is capable of exhibiting fluorescence, that is, of itself emitting electromagnetic radiation. It should be understood herein that suitable fluorescent materials may include solid, liquid or gaseous materials, without departing from the scope of the invention.

[0063] For example, in some embodiments of the laser cooling methods described herein, the fluorescent material may be a solid material including a host material doped with ions of a rare-earth element. Indeed, the benefits of using rare-earth doped in transparent host materials for laser cooling of solids have been known for several decades due, in part, to their high quantum efficiencies and narrow spectral lines. Another advantage of rare-earth ions lies in the fact that their optically active $4f$ electrons are shielded by the filled $5s$ and $5p$ outer shells, thereby limiting their interaction with the lattice of the host material surrounding the rare-earth ions and significantly reducing non-radiative multiphonon decay.

[0064] In the present description, the term “rare-earth element” is understood herein to encompass the lanthanides elements having atomic numbers from 57 through 71, preferably erbium (Er), thulium (Tm) and ytterbium (Yb). Likewise, the term “rare-earth ion” is understood to refer to an ion (i.e. a particle having a net electric charge) of a rare-earth element. In some embodiments, the rare-earth ions may be trivalent rare-earth ions, preferably Er^{3+} , Tm^{3+} and Yb^{3+} .

[0065] It will be understood that any suitable host material may generally be employed in embodiments of the laser cooling method 100. The host material should be optically transparent, that is, capable of transmitting photons with relatively little absorption and reflection at the wavelength of operation of a pump laser and emission radiation employed in the laser cooling method 100. For example, in some embodiments, the host material may be a transparent glass or crystal, for example fluoride or chloride glasses and crystals having low phonon energy, so as to further reduce non-radiative decay and hence increase internal quantum efficiency [see Equation (2)].

[0066] It will also be understood that characteristics of host material such as refractive index, chemical durability, mechanical and thermal properties should be considered when selecting an ion-host combination for the solid material to be cooled in embodiments of the laser cooling method **100**. For example, an appropriate host material should not, in some embodiments, be hygroscopic in order to avoid deterioration in the presence of water molecules, which would reduce internal quantum efficiency. Likewise, the host material should preferably have good hardness so as to provide easy processing thereof.

[0067] In what follows, two laser cooling methods will be described which may be used in the context of the present invention. In a first aspect of the invention, a pulsed laser beam is used to induce an anti-Stokes cooling of a fluorescent material in a regime of superradiance. In a second aspect of the invention, two laser beams are directed simultaneously on a sample of fluorescent material to produce both an anti-Stokes and an upconversion cooling cycle for inducing a cooling of the sample.

Method for Cooling a Fluorescent Material with Superradiance Fluorescence

[0068] According to one aspect of the invention, there is provided a first method **100** for cooling a fluorescent material. Referring to FIG. 3, there is shown a flow chart of an embodiment of the method **100**.

[0069] The method **100** according to this aspect of the invention generally relates to the laser cooling of fluorescent materials employing the optical phenomenon of superradiance to improve the efficiency of laser cooling in the anti-Stokes regime. More particularly and contrary to prior art methods of laser cooling with superradiance, the method **100** makes possible the use of a single pulsed pump laser beam at a pump wavelength longer than a mean fluorescence wavelength of the fluorescent material to be cooled, so as generate superradiant pulses without CW co-pumping.

[0070] As will be described in further detail below, embodiments of the method **100** involve is using a pulse of a pump laser beam to excite electrons of fluorescent material from the top of the ground-state manifold to the bottom of an excited manifold where phonons are absorbed, as shown in FIG. 4. The excited ions then correlate with each other and relax to the ground state as a coherent ensemble at an accelerated relaxation rate caused by radiation of a superradiant pulse. Hence, in the method **100** according to an aspect of the invention, a single pulsed pump laser source causes absorption of phonons, resulting in cooling, and, simultaneously, constitutes a source of accelerated relaxation rate, caused by radiation of a superradiant pulse. It will be understood that in the laser cooling method **100** described herein, no additional laser source that would generate phonons and result in heating of the system is necessary.

[0071] Still referring to FIG. 3, the laser cooling method **100** first involves a step **102** of providing a sample of the fluorescent material, the sample having an elongated light propagation direction.

[0072] FIG. 5 provides a schematic representation of an embodiment of the sample **20** of the fluorescent material to which the laser cooling method **100** may be applied. In this embodiment, the fluorescent material is a fluorozirconate $\text{ZrF}_4\text{—BaF}_2\text{—LaF}_3\text{—AlF}_3\text{—NaF}$ (ZBLAN) glass doped with trivalent ytterbium ions (Yb^{3+}). In other embodiments, the fluorescent material may be another fluoride glass doped with Yb^{3+} (e.g. Yb^{3+} :ZBLANP, Yb^{3+} :BIG, Yb^{3+} :ABCYS), a

fluoro-chloride glass doped with Yb^{3+} (e.g. Yb^{3+} :CBNZn), an oxide crystal doped with Yb^{3+} [e.g. Yb^{3+} :KGd(WO_4)₂, Yb^{3+} :KY(WO_4)₂, Yb^{3+} :YAG, Yb^{3+} :Y₂SiO₅], a fluoride crystal doped with Yb^{3+} (e.g. Yb^{3+} :BaY₂F₈, Yb^{3+} :YLF), a chloride crystal doped with Yb^{3+} (e.g. Yb^{3+} :K₂Pb₂Cl₅), a fluoride glass doped with Tm^{3+} (e.g. Tm^{3+} :ZBLAN), a fluoride crystal doped Tm^{3+} (e.g. Tm^{3+} :BaY₂F₈), a fluoro-chloride glass doped Er^{3+} (e.g. Er^{3+} :CNBZn) or a chloride crystal doped with Er^{3+} (e.g. Er^{3+} :K₂Pb₂Cl₅) [see, e.g., Table 1 in G. Nemova and R. Kashyap, Rep. Prog. Phys. vol. 73, p. 086501 (2010)]. In further embodiments, the fluorescent material may be ceramic glasses, crystals, polymers, semiconductors, is chalcogenide glasses, with nanoparticles or quantum dots. In still further embodiments, the fluorescent material may be a liquid or a gaseous material.

[0073] As used herein, the expression “elongated light propagation direction” may refer to the fact that the sample of the fluorescent material is geometrically elongated along one direction thereof. However, the expression “elongated light propagation direction” may also be used to encompass cases wherein the sample of the fluorescent material allows electromagnetic radiation to undergo multiple passes through the sample, thereby creating an effectively elongated sample along one direction thereof. This may be achieved, for example, by placing the sample in a resonant cavity or by exciting specific electromagnetic modes in the sample.

[0074] In the embodiment shown in FIG. 5, by way of example, the sample **20** is shaped as a cylinder of radius $r=0.5$ mm, length $L=5$ mm and aspect ratio $L/r=10$, so that the sample **20** may considered elongated along a direction **22** coinciding with the axis of the cylinder. The cylindrical sample **20** thus has an elongated light propagation along the axis thereof. In other embodiments, the sample may be shaped as a rectangular parallelepiped.

[0075] One skilled in the art will understand that the sample may have another shape than described herein without departing from the scope of the laser cooling method **100**, as long as it is elongated along one direction thereof or has an elongated light propagation direction as defined above. In this context, the expression “elongated sample” is understood to refer to a sample of a shape having a length significantly greater along one axis of an appropriate three-dimensional coordinate system.

[0076] In further embodiments, the sample of the fluorescent material may also be a sphere or a substantially spherical sample supporting whispering gallery modes, which are used to extend the sample in one dimension. As used herein, the expression is “whispering gallery modes” should be understood to refer to closed circular waves trapped by total internal reflection inside an axially symmetric dielectric body. Hence, due to the trapping and multiple reflections associated therewith, the excitation of whispering gallery modes in a spherical sample of fluorescent material may effectively produce an elongated light propagation direction in the sample.

[0077] Referring back to FIG. 3, in the providing step **102**, the fluorescent material making up the sample exhibits fluorescence at a mean fluorescence wavelength and is capable of entering a superradiance regime wherein superradiant pulses are emitted with a formation delay time.

[0078] In the present description, the term “fluorescence” is understood to refer to the emission of electromagnetic radiation by a substance that has absorbed electromagnetic radiation. A fluorescent material usually absorbs electromagnetic radiation in particular regions of the electromagnetic spec-

trum, thereby defining an absorption spectrum which is characteristic of this particular material. The fluorescent material may then re-emit electromagnetic radiation at different fluorescence wavelengths so as to define a corresponding fluorescence spectrum. It will be understood that fluorescence spectrum may, but need not, be similar to the absorption spectrum, and may comprise one or a plurality of emission bands of various strengths. By way of example, the spectra of absorption and emission cross-sections of Yb^{3+} ions in a ZBLAN host material have been presented by J. Parker et al., J. Appl. Phys. vol. 105, p. 013116 (2009), and is illustrated in FIG. 6 (PRIOR ART).

[0079] Furthermore, the term “mean fluorescence wavelength” is understood herein to refer to an appropriately averaged wavelength that accounts for the fluorescence spectrum of the fluorescent material. In particular, as described above, pumping the fluorescent material at a pump wavelength λ_p longer than the mean fluorescence wavelength λ_F is will yield anti-Stokes fluorescence emission and possibly optical refrigeration.

[0080] In embodiments of the laser cooling method 100 described herein and exemplified by the embodiment corresponding to the flow chart of FIG. 3, the optical cooling of the sample of the fluorescent material results from a process of superradiance. In the present description, the term “superradiance” refers to a process of spontaneous collective emission of coherent photons by an ensemble of excited particles coupled by electromagnetic radiation and noise field.

[0081] As a result of this collective effect, the relaxation time to the ground state of the ensemble of excited particles is shorter than the spontaneous relaxation time of a corresponding single excited particle. This spontaneous coherent emission of radiation constitutes a superradiant pulse, characterized in that all the energy stored in the sample is released in the form of coherent emitted light. A system exhibiting such a cooperative effect is referred to as being “superradiant” or to have entered a “superradiance regime”. The source of this coherence is the excited ions correlated over the electromagnetic field. It will also be understood by one skilled in the art that the superradiance regime does not involve stimulated emission, which is another source of coherent radiation.

[0082] The time needed for the superradiant pulse to form is referred to as the “formation delay time” of the superradiant pulse, which is denoted by the symbol τ_D . The formation delay time may equivalently be interpreted as the time in which the ensemble of excited particles is capable of entering a superradiance regime. It will be understood by one skilled in the art that no stimulated emission is involved in the superradiance process.

[0083] As mentioned above, it is known in the art that incoherent fluorescence in a fluorescent material made of rare-earth doped crystal or glass is a result of spontaneous relaxation of independent ions in a transparent host. It will thus be understood that, in embodiments of the laser cooling method 100 wherein the fluorescent material is a solid material doped with ions of a rare-earth element, the intensity I of this incoherent fluorescence is proportional to the number N of excited rare-earth ions in a sample of the solid material, that is, $I \sim N$. On the other hand, in his theoretical work on superradiance, Dicke considered the entire collection of two-level atoms of sample of the solid material as a single quantum-mechanical system [see R. H. Dicke, Phys. Rev. vol. 93, p. 99 (1954)]. Moreover, Dicke found that under certain conditions to be discussed below, the atoms cooperate and relax to the

ground state in a time τ_{sR} much shorter than the spontaneous relaxation time τ_s , associated with incoherent fluorescence, namely that $\tau_{sR} \approx \tau_s/N$. As a result, the intensity of radiation in the superradiance regime is shown to be proportional to the square of the number of excited atoms, that is, $I \sim N^2$.

[0084] It must be noted that some conditions should be fulfilled by the size, shape and physical properties of the sample of the fluorescent material for superradiance to be achieved according to the laser cooling method 100. For example, as in the embodiment of FIG. 5, the sample 20 should preferably be greatly extended along one direction 22 thereof to allow the formation of a superradiant pulse 28. Indeed, since the superradiant pulse is correlated and has a narrow angle of emission, an elongated sample should preferably be used to allow emission in that direction, principally by exciting all the available ions.

[0085] Furthermore, as described in further detail below, the time of flight τ of a photon through the sample 20 should preferably remain short in comparison with the other characteristic times involved in the formation of the superradiant pulses 28. As known in the art, the time of flight τ of a photon along the elongated direction 22 (i.e. length is L) of the sample 20 shown in FIG. 5 is given by $\tau = Ln/c$, where n is the refractive index of the fluorescent material, which is equal to $n=1.5$ in this particular embodiment, and $c \approx 3 \times 10^8$ m/s is the speed of light in vacuum. Hence, as described below, the size of and refractive index of the fluorescent material should be selected appropriately in the laser cooling method 100 described herein.

[0086] Additionally, since superradiance is a cooperative process, the total concentration N_T of rare-earth ions in the host material (i.e. both ground-state and excited-state ions) should be high. Preferably, the total concentration N_T of rare-earth ions in the host material is selected to be about 10^9 ions/ μm^3 . For example, in the embodiment of FIG. 5, the sample 20 is a doped with Yb^{3+} ions at a concentration N_T equal to 1.45×10^9 ions/ μm^3 .

[0087] Referring to FIG. 3, the laser cooling method 100 next involves a step 104 of generating a pump laser beam 24 including laser pulses 26, as illustrated in FIG. 5. Indeed, it is known in the art that optical cooling should involve laser radiation, so as to provide an excitation source with a sufficiently narrow spectral power distribution.

[0088] In the present description, the term “laser beam” is understood to refer to a high-intensity, spatially-coherent and nearly monochromatic beam of electromagnetic radiation. The electromagnetic radiation may be photons of energy encompassing the visible, infrared and ultraviolet portions of the electromagnetic spectrum. As discussed below, the laser beam may be characterized by several optical characteristics, including a pump wavelength λ_p and a pump power P_p . The term “pump” is understood herein to refer to the fact that, as described below, the laser cooling method 100 employs the laser beam as an excitation source for inducing atomic electron transitions in a sample of rare-earth-doped host material.

[0089] As known in the art, the pump laser beam according to the laser cooling method 100 may be produced by a laser source, which may be embodied, for example, by an electrically-pumped semiconductor lasers, an optically-pumped solid-state laser, an optical fiber laser, a solid state amplification system, an optical parametric amplification system, a fiber amplification system, a chirped pulse amplification system, a combination of these lasers and amplification systems, or the like.

[0090] The expression “laser pulses” is understood herein to refer to the discrete onset of laser radiation separated by an inter-pulse period where light is absent or negligible. Any given laser pulse has optical characteristics which define it with respect to time, space and wavelength, for example a pulse duration τ_p and a pulse shape.

[0091] In the present description, the expression “pulse duration” generally refers to the period of time between the beginning and the end of an individual pulse. Several conventions may be used to determine the moment at which a laser pulse begins and ends, as will be readily understood by one skilled in the art. For example, it may be determined accordingly to a given fraction, such as 50% or $1/e^2$ or any other fraction, of the maximum intensity of a simple pulse temporal profile. It will be understood herein that both the laser pulses composing the pump laser beam and the superradiant pulses composing the superradiance regime may be assigned a pulse duration.

[0092] The expression “pulse shape” is used to refer herein to the shape of the temporal profile of the laser pulses, that is, the form obtained when the pulse amplitude or intensity is plotted as a function of time. For example, in the embodiment of the method **100** shown in FIG. 5, the laser pulses **26** of the pump laser beam **24** are rectangular in shape.

[0093] It will be understood that, in addition to the conditions mentioned above regarding the size, shape and physical properties of the sample of the fluorescent material, achieving superradiance also involves conditions on the pulse duration τ_p of the laser pulses composing the pump laser beam. All these conditions have been presented and discussed by Dicke and may be summarized by the following inequalities:

$$\tau < \tau_c < \tau_s, \tau_2, \quad (6)$$

$$\tau_p < \tau_D. \quad (7)$$

[0094] Here, τ , τ_p and τ_D have been introduced above and denote the time of flight of a photon through the sample of the fluorescent material, the pulse duration of the pump laser pulses and the formation delay time of a superradiant pulse, respectively, while τ_c is the correlation self-formation time in the fluorescent material characterizing the full width at mid-height of the intensity of the superradiant pulse, τ_s is the spontaneous relaxation time characterizing incoherent fluorescence in the fluorescent material, τ_2 is the time of phase irreversible relaxation.

[0095] On the one hand, the left inequality in Equation (6) indicates that the propagation time τ of photons in the sample of the fluorescent material should be shorter than the characteristic times thereof, that is, τ_c , τ_s , and τ_2 . On the other hand, the right inequality in Equation (6) indicates that the formation of a superradiant pulse in the sample should to be a faster process than the process of spontaneous relaxation resulting in incoherent anti-Stokes fluorescence emission. It will be understood herein that as soon as the left inequality in Equation (6) is satisfied, the sample becomes essentially free from re-absorption since all generated photons leave the sample.

[0096] Meanwhile, the inequality of Equation (7), which is illustrated in FIG. 13, indicates that a laser pulse of the pump laser beam should have a pulse duration τ_p that is shorter than the formation delay time τ_D of a superradiant pulse or, in other words, that the pump laser pulses and the superradiant pulses should not or minimally overlap in time.

[0097] It is of interest to note that the process of formation of a superradiant pulse is entirely different from the process of

formation of the amplified signal in a laser system, which is based on stimulated emission, although both cases result in coherent radiation emission.

[0098] Referring to FIG. 3, the generating **104** first involves a substep **106** of selecting a pump wavelength of the pump laser beam that is longer than the mean fluorescence wavelength of the fluorescent material.

[0099] As one skilled in the art will understand, this substep **106** ensures that anti-Stokes fluorescence emission is generated within the sample of the fluorescent material. For example, in the case of the embodiment shown in FIG. 5, the wavelength λ_p of the pump laser beam **24** is equal to 1015 nm, which is longer than the mean fluorescence wavelength $\lambda_F=999$ nm of the Yb^{3+} ions in the ZBLAN host material. Of course, depending on the fluorescence emission spectrum of the fluorescent material to be laser cooled by the method **100** described herein, different values for the wavelength of the pump laser beam may be selected.

[0100] Referring back to FIG. 3, the generating **104** then involves a substep **108** of selecting a pump power of the pump laser beam so as to reach the superradiance regime of the fluorescent material.

[0101] In general, the pump power of the pump laser beam needs to be within a certain range of values for the fluorescent material to emit superradiant pulses. More particularly, the pump power should be high enough to trigger the onset of superradiance, but not so high as to generate non-linear optical effects in the fluorescent material to be cooled. Preferably, the pump power of the pump laser beam is selected to be of the order of several hundred watts. For example, in the embodiment of FIG. 5, the pump power P_p of the pump laser beam **24** is equal to 433.5 W.

[0102] It should also be mentioned that varying the pump power value of the pump laser beam may have an impact on the value of some of the characteristic times of the fluorescent material involved in the inequalities of Equations (6) and (7). In particular, the formation delay time τ_D and the correlation self-correlation time τ_c of the superradiant pulses change according to the value of the pump power P_p since the number of excited rare-earth ions in the sample of the fluorescent material participating in the formation of a superradiant pulse depends itself on P_p . In this regard, FIGS. 9 and 10 show that both τ_D and τ_c decreases with increasing value of P_p . Hence, it will be understood that the value of the pump power of the pump laser beam should preferably be selected so that the corresponding values of τ_D and τ_c fulfill Equations (6) and (7), which should be satisfied in order for the fluorescent material to enter the superradiance regime.

[0103] The generating **104** next involves a substep **110** of selecting a pulse duration of the laser pulses that is shorter than the formation delay time of the superradiant pulses. It will be understood that this substep corresponds to the fulfillment of the condition $\tau_p < \tau_D$ given in Equation (7).

[0104] For example, in rare-earth-doped solid materials, the formation delay time τ_D of superradiant pulses is typically of the order of tens of nanoseconds so that, in such embodiments, the pulse duration τ_p of the laser pulses should be shorter than that. However, it will be understood that in order for the pump power PP of the pump laser beam to be sufficiently high for superradiance to be achieved, the pulse duration τ_p may preferably be of the order of tens of nanoseconds, rather than in the picosecond and femtosecond range. In the embodiment of FIG. 5, the pulse duration τ_p of the laser pulses **26** is equal to 10 ns.

[0105] The method **100** further then a step **112** of directing the laser pulses of the pump laser beam onto the sample of the fluorescent material along the elongated light propagation direction thereof so as to produce the superradiant pulses in anti-Stokes process inducing a cooling of the sample. In the embodiment of FIG. 5, the directing step **112** includes directing the laser pulses **26** of the pump laser beam **24** along the extended direction **22** of the sample **20** of the fluorescent material due to the low emission angle of the superradiant pulses. Preferably, and in order to provide a more efficient cooling, the laser cooling method **100** includes a step of mounting the sample of the fluorescent material in a vacuum chamber prior to directing the laser pulses thereonto.

[0106] In general, it will be understood that in the directing step **112**, the pulses of the pump laser beam having parameters selected in the generating step **104**, illuminates the sample of the fluorescent material in order to achieve coherent anti-Stokes fluorescence via emission of superradiant pulses, thereby cooling the sample. In the following, the formation of superradiant pulses upon directing the laser pulses of the pump laser beam onto the sample according to embodiments of the laser cooling method **100** will be described in detail. In particular, the improved efficiency of the cooling cycle provided by embodiments of the method **100** over a traditional anti-Stokes cooling cycle will be discussed.

[0107] It will be understood that this description is meant to provide assistance in comprehending the physical phenomena underlying the method **100** as understood by the inventors, and is in no way meant to be limitative to the scope of the present invention.

[0108] As described above, the process of forming a superradiant pulse begins as incoherent fluorescence, wherein rare-earth ions in the host material do not interact with each other. Gradually, interactions between the ions through electromagnetic radiation and noise field increase and lead to a correlation of their dipole moments, which reaches a maximum at a time τ_D corresponding to the formation delay time of the superradiant pulse. It is known in the art that in the superradiance regime, a major proportion of the power emitted by superradiance is radiated as highly directional emission of superradiance pulses along or close to the direction along which the sample is most extended. This is illustrated in the embodiment of FIG. 5, wherein the superradiance pulses **28** exhibit a sharp directionality in space along the extended direction **22** of the sample **20** of the fluorescent materials and are observed simultaneously both along and against the direction of propagation of the pump laser beam **24**.

[0109] The instantaneous power of the superradiant signal is given by the following equation [see V. V. Samartsev and A. A. Kalachev, Hyp. Interact. vol. 135, p. 257 (2001)]:

$$P(t) = \frac{hc}{\tau_s \lambda_F} \mu \frac{N^2}{4} \text{sech}^2\left(\frac{t - \tau_D}{2\tau_c}\right), \quad (8)$$

where t is the time, λ_F is the mean fluorescence wavelength, N is the number of excited rare-earth ions in the sample of the fluorescent material, and μ is a geometry-dependent parameter of the sample which has been investigated in the art [see T. R. Gosnell, Opt. Lett. vol. 24, p. 1041 (1999)]. In par-

ticular, for a cylindrically-shaped sample **20**, such as in the embodiment shown in FIG. 5, the geometry-dependent parameter is given by

$$\mu = \frac{\lambda_F^2}{2A_{eff}(1 + \sqrt{1 + F^{-2}})}, \quad (9)$$

where A_{eff} is an effective mode area and $F = A_{eff}/(\lambda_F L)$ with L being the length of the sample.

[0110] It will be understood that Equation (8) described the evolution of the power $P(t)$ of the superradiant pulse as a function of time. In particular, FIG. 8 shows a graph of $P(t)$ normalized to the maximum value thereof, corresponding to the sample **20** of ZBLAN doped with Yb^{3+} in the embodiment of FIG. 5. It may be seen that $P(t)$ is maximum at a time corresponding to the formation delay time of the superradiant pulse, which is equal to $\tau_D \approx 14$ ns in FIG. 8 and satisfies Equation (7) since the pulse duration τ_p of the laser pulses **26** is equal to 10 ns in this embodiment. Furthermore, the correlation self-formation time in the fluorescent material corresponds to the full width at mid-height of $P(t)$, which is equal to $\tau_c \approx 1$ ns in FIG. 8. This value for τ_c satisfies Equation (6) since the time of spontaneous relaxation $\tau_s \approx 1.9$ ms while the time of flight of a photon through the sample **20** $\tau = Ln/c \approx 25$ ps.

[0111] Then, the total energy radiated from the sample of the fluorescent material via the emission of a superradiant pulse may be obtained by integrating Equation (8) over time, which yields

$$E_{SR} = \frac{hc}{\lambda_F} \frac{\tau_c}{\tau_s} \mu \frac{N^2}{2} \left[1 + \tanh\left(\frac{\tau_D}{2\tau_c}\right) \right]. \quad (10)$$

[0112] In order to apply the model used by Dicke to the embodiment of FIG. 5 to which the laser cooling method **100** illustrated in FIG. 3 is applied, the trivalent ytterbium ions Yb^{3+} of the Yb^{3+} :ZBLAN sample **20** may be described with two-level model for absorption and emission processes between the ground-state $^2F_{7/2}$ and the excited-state $^2F_{5/2}$ manifolds. In this case, it has been shown by Dicke that the correlation self-formation time τ_c and the formation delay time τ_D may be calculated using the following relations

$$\tau_c = \frac{\tau_s}{N\mu}, \quad (11)$$

$$\tau_D = \tau_c \ln(N\mu). \quad (12)$$

[0113] Moreover, the population density N_2 in the excited state manifold changes with time and should satisfy the relation:

$$\frac{dN_2}{dt} = \frac{P_p(t)}{A_{eff}} \frac{\lambda_p}{hc} [\sigma_{abs}(\lambda_p)N_1(t) - \sigma_{es}(\lambda_p)N_2(t)] - \frac{N_2(t)}{\tau_s} \quad (13)$$

where $P_p(t)$ is the instantaneous pump power at the pump wavelength λ_p at time t , $\sigma_{abs}(\lambda_p)$ and $\sigma_{es}(\lambda_p)$ respectively the absorption and emission cross-sections at the pump wave-

length λ_p , respectively, and $N_1(t)$ is the population density of the ground-state manifold at time t . It will be understood that the total density N_T of Yb^{3+} ions is constant in time and is given by $N_1(t) + N_2(t) = N_T$.

[0114] Referring back to the embodiment of FIG. 5, the pump laser beam 24 has a pump power P_p and includes laser pulses 26 having a pulse duration τ_p and a rectangular pulse shape. In this particular case, the number of excited Yb^{3+} ions in the sample 20 of length L is given by

$$N = L \sigma_{abs} N_T \tau_p P_p \frac{\lambda_p}{hc}. \quad (14)$$

[0115] For this particular embodiment, with a pump power $P_p = 433.5$ W and a pulse duration $\tau_p = 10$ ns, the number of the trivalent ytterbium ions Yb^{3+} in the sample 20 of Yb^{3+} :ZBLAN participating in the cooling process with superradiance is approximately equal to $N = 6 \times 10^{12}$ ions.

[0116] Then, due to the process of thermalization mentioned above, some of the excited electrons may be promoted from the bottom to the top of the excited-state manifold (e.g. $^2F_{5/2}$ for the exemplary embodiment of FIG. 5) by absorbing the energy of phonons, which, as known in the art, are responsible for heat generation in the sample, as illustrated schematically in the inset of the graph shown in FIG. 6 (PRIOR ART). As a result, anti-Stokes fluorescence emission of photons may follow with mean photon energy $E_F = h\nu_F$, where $\nu_F = c/\lambda_F$ is the mean frequency of anti-Stokes photons, which is higher than the energy E_p of the laser pulses of the pump laser beam. As will be understood by one skilled in the art, this anti-Stokes emission may remove energy from the sample and realize an optical cooling thereof.

[0117] As known in the art, the time in which energy is removed from the sample via incoherent anti-Stokes fluorescence cooling is of the order of τ_s , which corresponds to the time of spontaneous relaxation. Hence, the emission power of incoherent anti-Stokes fluorescence is equal to

$$P_{SP} = \frac{Nhc}{\tau_s \lambda_F}. \quad (15)$$

[0118] On the other hand, considering Equation (10), the power P_{SR} removed from the sample of the fluorescent material by the superradiant pulse, which corresponds to the energy E_{SR} removed from the sample per cooling cycle, is given by

$$P_{SR} = \frac{hc}{\lambda_F} \frac{\tau_c}{\tau_s} \frac{1}{\tau_{cool}^{SR}} \mu \frac{N^2}{2} \left[1 + \tanh\left(\frac{\tau_D}{2\tau_c}\right) \right], \quad (16)$$

where τ_{cool}^{SR} is the time duration of the superradiant cooling cycle, which is equal to the sum of the pump pulse duration τ_p and the formation delay time τ_D of the superradiant pulses.

[0119] Comparing Equations (15) and (16), one may calculate the ratio C of the power P_{SR} removed from the sample via superradiance to the power P_{SP} removed from the sample via incoherent anti-Stokes fluorescence, which is given by

$$C = \frac{\tau_c}{\tau_{cool}^{SR}} \mu \frac{N}{2} \left[1 + \tanh\left(\frac{\tau_D}{2\tau_c}\right) \right]. \quad (17)$$

[0120] The parameter C thus characterizes the increase in the radiative relaxation rate with superradiance with respect to the radiative relaxation rate with incoherent anti-Stokes fluorescence. Moreover, one may also define an effective radiative relaxation time as $\tau_s = \tau_s / C$, so as to characterize the rate of electron relaxation in the superradiance regime compared to the rate of spontaneous relaxation τ_s .

[0121] Hence, if $C > 1$, then $\tau_s < \tau_s$ and the energy leaves the sample faster with the laser cooling method 100 with superradiance according to embodiments of the invention than traditional cooling experiments based on the emission of incoherent anti-Stokes fluorescence. For example, in the embodiment of FIG. 5, the sample 20 of ZBLAN doped with Yb^{3+} with the material and geometrical properties given above has a value of $C = 1.4 \times 10^5$ when the pump power $P_p = 433.5$ W. The behavior of C as a function of P_p is illustrated in FIG. 11. As a result, the energy removed from the sample 20 of Yb^{3+} :ZBLAN by the superradiant pulses 28 is, at each second of the cooling cycle, larger by a factor of about 10^5 than the energy that would be removed with incoherent anti-Stokes fluorescence. The laser cooling method 100 may thus yield a significant increase (i.e. by a factor of about 10^5 in some embodiments) of the radiative relaxation rate compared to other laser cooling methods known in the art.

[0122] The cooling efficiency per cooling cycle of superradiant cooling may be determined from the ratio of the energy E_{SR} removed from the sample 20 by a superradiant pulse 28 to the energy of a pulse 26 of the pump laser beam 24, during one cooling cycle. Using Equation (10) and the fact that the energy absorbed by the sample from the laser pulse 26 is equal to $Nh\nu_p$, the superradiant cooling efficiency per cooling cycle is given by

$$\eta_{cool}^{SR} = \frac{\nu_F}{\nu_p} \frac{\tau_{cool}^{SR}}{\tau_s} C - 1 \quad (18)$$

[0123] Referring to FIG. 7, there are shown computer simulations made from Equation (18). The superradiant cooling efficiency per cooling cycle provided by the laser cooling is method 100 according to embodiments of the invention is compared with the anti-Stokes cooling efficiency per cooling cycle, which may be expressed as $\rho_{cool}^{SP} = \nu_F/\nu_p - 1$ and has been calculated by Luo et al. and by Allain et al. [see X. Luo et al. Opt. Lett. vol. 23, p. 639 (1998) and J. Y Allain et al., Electron. Lett. vol. 28, p. 988 (1992)]. It is to be noted that in both cases, non-radiative relaxations in the host have not been taken into account.

[0124] Upon examining FIG. 7, one skilled in the art will recognize that, in this embodiment, heat removal with the laser cooling method 100 with superradiance described herein is about twice as effective as incoherent anti-Stokes cooling. However, it should be emphasized that since the time duration τ_{cool}^{SR} of the superradiant cooling cycle is shorter by a factor τ_{cool}^{SR}/τ_s than the time of the traditional anti-Stokes cooling cycle, which in some embodiments may be as large as 10^5 . Hence, the cooling efficiency per unit with superradiance

may increase considerably compared to that provided by incoherent anti-Stokes fluorescence.

[0125] It should also be noted that in order to generate superradiant pulses, the number of N excited ions in the sample of the fluorescent material should be in excess of a threshold value N_{th} , which may be calculated by using the right in inequality of Equation (6) and by taking into account that $\tau_c = \tau_s / (\mu N)$, such that:

$$N_{th} > \frac{\tau_s}{\tau_2 \mu t}. \quad (19)$$

[0126] According to the laser cooling method **100** of the present invention, this threshold value may preferably be reduced by increasing the pump power P_p of the pump laser beam or the total density N_T of the rare-earth ions in the host material. Furthermore, N_{th} also decreases when the temperature of the sample decreases since τ_2 increases as the temperature of the sample drops.

[0127] In summary the coherence introduced in the cooling process with a superradiant pulse permits a noticeable increase of the cooling rate, thus increasing the efficiency of the laser cooling method **100** in comparison with traditional cooling with anti-Stokes fluorescence of low phonon hosts.

[0128] Following the traditional experiments devoted to laser cooling with incoherent anti-Stokes fluorescence, one may consider that in the embodiment shown in FIG. 5, the sample **20** of $\text{Yb}^{3+}:\text{ZBLAN}$ that is cooled with superradiance is mounted in a vacuum chamber (not shown) and only the radiative heat load is present. In this case, the temperature of the sample of the fluorescent material may be calculated from the equation:

$$2\pi r L \epsilon \sigma_B (T_{amb}^4 - T_s^4) = P_{cool}^{SR}, \quad (20)$$

where ϵ is the hemispherical emissivity of the sample, $\sigma_B = 5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ is the Stefan-Boltzmann constant, T_{amb} is the ambient temperature in the vacuum chamber, T_s is the sample temperature to be determined and P_{cool}^{SR} is the cooling power with SR.

[0129] The cooling power per single pump pulse is the difference between the energy Nhc/λ_p absorbed by the sample of the fluorescent material from the laser pulse of the pump laser beam and the energy E_{SR} of the superradiant pulse radiated by the sample [see Equation (10)], divided by the time duration $\tau_{cool}^{SR} = \tau_p + \tau_D$ of the cooling cycle, which is equal to the sum of the laser pulse duration τ_p and the formation delay time of the superradiant pulse τ_D . The evolution of the number of pump pulses as a function of its sample temperature T_s is illustrated in FIG. 12, again for a peak power of the pump laser $P_p = 433.5 \text{ W}$ and a pulse duration $\tau_p = 10 \text{ ns}$.

[0130] The cooling rate per cycle in the superradiance regime may be described by the expression $P_{cool}^{SR}/\tau_{cool}^{SR}$, which represents the ratio of the cooling power P_{cool}^{SR} leaving the sample of the fluorescent material during a cooling cycle in the superradiance regime to the duration τ_{cool}^{SR} of the cooling cycle. Similarly, when a sample is pumped with a CW laser so as to generate optical via incoherent anti-Stokes fluorescence, the duration of the cooling cycle corresponds to the lifetime τ_s of the excited level and the cooling rate per cycle is given by P_{cool}^{SR}/τ_s . The cooling power of incoherent anti-Stokes fluorescence may then be calculated with the following expression [see X. Luo et al., Opt. Lett. vol. 23, p. 639 (1998)]:

$$P_{cool}^{SP} = VN \frac{\left(\frac{\lambda_p}{\lambda_F} - 1\right) I_s \sigma_{abs}(\lambda_p)}{\left[1 + \frac{\sigma_{se}(\lambda_p)}{\sigma_{abs}(\lambda_p)}\right] + I_s \frac{A_{eff}}{P_p}} \quad (21)$$

where $I_s = hc/[\tau_s \lambda_p \sigma_{abs}(\lambda_p)]$, and V is the volume of the sample of the fluorescent material.

[0131] From Equation (21), it will be understood by one skilled in the art that the cooling rate P_{cool}^{SR}/τ_s with incoherent anti-Stokes fluorescence depends on the value of the pump power P_p of the pump laser beam, that is, P_{cool}^{SR}/τ_s increases as P_p increases. FIG. 7 illustrates the variation of the cooling rate $P_{cool}^{SR}/\tau_{cool}^{SR}$ and P_{cool}^{SR}/τ_s as a function of the pump power P_p for cooling with superradiance and incoherent anti-Stokes fluorescence, respectively. As can be understood by one skilled in the art upon examining FIG. 7, the cooling rate $P_{cool}^{SR}/\tau_{cool}^{SR}$ with superradiance exceeds considerably the cooling rate P_{cool}^{SR}/τ_s with the anti-Stokes fluorescence. In particular, although both cooling rates increase with increasing pump power, the slope is greater with is superradiance cooling. In particular, in the superradiance regime, the formation delay time τ_D of the superradiant pulse, and, thus duration $\tau_{cool}^{SR} = \tau_p + \tau_D$ of the cooling cycle, decreases with increasing pump power, as shown in FIG. 9, thereby providing a steeper slope for $P_{cool}^{SR}/\tau_{cool}^{SR}$ as a function of P_p .

[0132] As mentioned above, an ion (e.g. a rare-earth ion) that has been promoted to an excited state may decay non-radiatively via interactions with optical phonons of the host material. In the context of laser cooling of materials, non-radiative decay caused undesired heating of the sample. The competition between radiative and non-radiative decays may be characterized by the internal quantum efficiency η of Equation (2), wherein the non-radiative rate W_{nr} due to multiphonon transition given above in Equation (4) can be rewritten as

$$W_{nr} = \frac{W_0}{[1 - \exp(-E_{ph}/k_B T)]^{n_p}}, \quad (22)$$

where $W_0 = B \exp(-\alpha \Delta E_8)$ is the spontaneous transition rate $T=0 \text{ K}$ due to the zero-point fluctuations of the phonon field, E_{ph} is the dominant phonon energy and ΔE is the energy gap that is bridged by the emission of n_p phonons. As mentioned above, the internal quantum efficiency η reduces the cooling efficiency provided by the sample of the sold material to $\eta_{cool} = \eta \lambda_p / \lambda_F - 1$ [see Equation (3)].

[0133] In the superradiance regime, since the radiative relaxation time $\tau_s = \tau_s / C$ decreases significantly compared to the spontaneous relaxation time τ_s , the radiative relaxation is rate W_r increases accordingly. As previously mentioned, in the case of the sample **20** of $\text{Yb}^{3+}:\text{ZBLAN}$ considered in the embodiment of FIG. 5, the radiative relaxation rate $1/\tau_s$ increases approximately by a factor of 10^5 in the superradiance regime.

[0134] As consequence, the laser cooling method **100** with superradiance according to embodiments of the invention may increase the internal quantum efficiency η given in Equation (3) significantly compared to the case of traditional cool-

ing with anti-Stokes fluorescence and this, independently of the nature of the host material.

[0135] It should also be noted that, in general, the radiative relaxation rate Γ_N , only slightly depends of the nature of host material in comparison with the non-radiative relaxation rate W_{nr} . As a result, the laser cooling method **100** with superradiance of the present invention may allow using host materials characterized by a considerably higher value for the non-radiative rate W_{nr} , and thus maximum phonon energy $\hbar\omega_{max}$, than traditional hosts used for anti-Stokes fluorescence cooling, while still maintaining a suitably high value for the internal quantum efficiency η , as may be understood from Equation (2). Indeed, in the superradiance regime, the condition given in Equation (5) is relaxed as higher phonon energy host materials may be used, and bridging the gap with fewer phonons may be allowed. It will be understood that even though the probability for the transitions increase exponentially, the probability of multiphonon absorption decreases as an exponential function of the number of phonons n_p [see, e.g., Equation (22)].

[0136] For example, the laser cooling method **100** with superradiance according to embodiments of the invention may allow cooling down a sample composed of a silica host doped with rare-earth ions and having a maximum phonon energy $\hbar\omega_{max} \approx 1100 \text{ cm}^{-1}$ (or other rare-earth-doped hosts with similar maximum phonon energies) with an internal quantum efficiency η that is similar to that observed in cooling of rare-earth-doped low-energy-phonon host with incoherent anti-Stokes fluorescence.

[0137] Furthermore, as known in the art, laser cooling of rare-earth-doped solids with incoherent anti-Stokes fluorescence ceases at about 77 K since, as known in the art, the phonon number decreases exponentially with decreasing temperature. On the contrary, due to the considerably high rate of radiation de-excitation of superradiant pulses, the embodiments of the laser cooling method **100** may break this limitation so that rare-earth-doped solid materials may be laser cooled below 77 K. It should also be emphasized that an important feature of the laser cooling method **100** is the recognition that the increased relaxation rate achievable in the superradiance regime plays a role in accelerating the cooling process in comparison to traditional laser cooling methods known in the art and based on incoherent anti-Stokes fluorescence.

[0138] Additionally, the laser cooling method **100** described herein opens up new possibilities for designing entirely solid-state optical coolers since, as shown in FIG. 5, the superradiance regime facilitates removal from the sample **20** of the heat extracted thereto due to the high directionality of the emitted superradiant pulses **28** along the elongated direction **22**. In particular, the laser cooling method **100** allows for a significant reduction of the risks of re-absorbing energy, and thus of re-heating the sample **20**, in comparison to traditional anti-Stokes fluorescence cooling, wherein fluorescence is emitted uniformly in all directions over a solid angle of 4π .

[0139] Finally, in embodiments where the fluorescent material is a rare-earth-doped host material, the laser cooling method **100** described herein broadens the range of host materials that can be used for laser cooling to host materials having a higher maximum phonon energy (e.g. silica, polymers, semiconductors, borosilicate glasses and other crystals

with high phonon energies), which have been so far considered unsuitable as rare-earth-doped hosts for laser cooling applications.

Method for Cooling a Fluorescent Material Using Two Simultaneous Cooling Cycles

[0140] According to another aspect of the invention, there is provided a second method **200** for cooling a fluorescent material. Referring to FIG. 14, there is shown a flow chart of an embodiment of the method **200**.

[0141] The method **200** according to this aspect of the invention generally relates to the laser cooling of fluorescent materials combining simultaneously a traditional anti-Stokes cooling cycle and an upconversion cooling cycle, in such a way as to help to overcome the self-termination effects that may present in either of these two cooling cycles when used on its own.

[0142] As mentioned before, the traditional cooling cycle is based on the emission of incoherent anti-Stokes fluorescence involving the emission of photons having higher energy than the photons absorbed from an excitation pump source. Hence, net anti-Stokes fluorescence may cause removal of energy from an illuminated material and, as a consequence, its refrigeration.

[0143] As also previously mentioned, the upconversion cooling cycle may rely on the infrared-to-visible upconversion process which is often found in rare-earth-doped low-phonon-energy host material due to the reduced multiphonon transition thereof. As understood herein, the term “upconversion” broadly refers to a process by which a material emits light with photon energies higher than those of the light generating the excitations. For example, in the infrared-to-visible upconversion process, at least two low-energy infrared photons are required to generate one high-energy visible photon. In upconversion fluorescence, at least two photons are absorbed during the excitation process of an electron, such that the emitted photon resulting from the de-excitation of the electron has a shorter wavelength than the absorbed photons. Hence, these excited-states levels constitute reservoirs of electrons that may be further excited by absorbing other photons.

[0144] As one skilled will understand, upconversion may be accomplished by several multiphoton mechanisms. As used herein, the expression “multiphoton absorption” is understood to refer to a process by which an electron in a material is excited by more than one photon (i.e. two or more) from a single pump source. For example, one mechanism known as excited state absorption (ESA) involves sequential absorption of pump photons. A first absorption typically leads to some metastable excited level with a relatively long lifetime. Then, an ion that has been excited to that metastable level is promoted into a higher excited level by at least one other photon from where it later decays spontaneously. As known in the art, ESA typically involves high pump power values, but not necessarily high doping concentrations.

[0145] Another mechanism, referred to as energy-transfer upconversion (ETU), involves energy transfer between two different ions in the material. In this case, two electrons of two different ions interact with each other and, as a result, one of them decays to a lower lying state while the other is promoted to a higher energy state. As opposed to ESA, ETU generally involves high doping concentrations.

[0146] In a further mechanism, multiphoton absorption may consist in the excitation of an electron by the absorption

of two or more photons that allow this electron to acquire the energy corresponding to the energy difference between two electronic levels by going through intermediate virtual levels.

[0147] Referring to FIG. 14, the laser cooling method 200 first involves a step 202 of providing a sample of the fluorescent material, the fluorescent material having an absorption spectrum comprising at least one absorption band, each of the at least one absorption band having a corresponding maximum absorption wavelength.

[0148] As discussed above, the laser cooling method 200 may be employed for cooling a fluorescent material that may be a solid material composed of a rare-earth-doped host material. The rare-earth ions may be trivalent rare-earth ions, preferably Er^{3+} , Tm^{3+} and Yb^{3+} . Likewise, the host material may be a transparent glass or crystal, for example fluoride or chloride glasses and crystals having low phonon energy.

[0149] In an embodiment of the method 200, the fluorescent material is a potassium-lead chloride host crystal KPb_2Cl_5 doped with trivalent erbium ions (Er^{3+}), which is known as a particularly low-phonon-energy crystal (e.g. the maximum phonon energy is about 203 cm^{-1}). In other embodiments, the fluorescent material may be selected from other rare-earth-doped host materials in which net laser cooling has been observed.

[0150] In other embodiments, the fluorescent material may be a fluoride glass doped with Yb^{3+} (e.g. $\text{Yb}^{3+}:\text{ZBLAN}$, $\text{Yb}^{3+}:\text{ZBLANP}$, $\text{Yb}^{3+}:\text{BIG}$, $\text{Yb}^{3+}:\text{ABCYS}$), a fluoro-chloride glass doped with Yb^{3+} (e.g. $\text{Yb}^{3+}:\text{CBNZn}$), an oxide crystal doped with Yb^{3+} [e.g. $\text{Yb}^{3+}:\text{KGd}(\text{WO}_4)_2$, $\text{Yb}^{3+}:\text{KY}(\text{WO}_4)_2$, $\text{Yb}^{3+}:\text{YAG}$, $\text{Yb}^{3+}:\text{Y}_2\text{SiO}_5$], a fluoride crystal doped with Yb^{3+} (e.g. $\text{Yb}^{3+}:\text{BaY}_2\text{F}_8$, $\text{Yb}^{3+}:\text{YLF}$), a chloride crystal doped with Yb^{3+} (e.g. $\text{Yb}^{3+}:\text{KPb}_2\text{Cl}_5$), a fluoride glass doped with Tm^{3+} (e.g. $\text{Tm}^{3+}:\text{ZBLAN}$), a fluoride crystal doped with Tm^{3+} (e.g. $\text{Tm}^{3+}:\text{BaY}_2\text{F}_8$), or a fluoro-chloride glass doped with Er^{3+} (e.g. $\text{Er}^{3+}:\text{CNBZn}$) [see, e.g., Table 1 in G. Nemova and R. Kashyap, Rep. Prog. Phys. vol. 73, p. 086501 (2010)].

[0151] In further embodiments, the fluorescent material may be ceramic glasses, crystals, is polymers, semiconductors, chalcogenide glasses, with nanoparticles or quantum dots. In still further embodiments, the fluorescent material may be a liquid or a gaseous material.

[0152] In the present description, the term “absorption spectrum” is understood to refer to a spectrum of radiant energy over a range of wavelengths whose intensity at each wavelength corresponds to a measure of the fraction of incident radiation that is absorbed by a material. As known in the art, the absorption spectrum depends mostly on the composition of the material since absorption is more likely to take place at photon energies corresponding to the energy difference between two energy levels in the material. Likewise, the expression “absorption band” is understood herein to refer a range of energies or wavelengths in the absorption spectrum which are capable of exciting a particular transition in material. Moreover, the “maximum absorption wavelength” of a particular absorption band refers to the wavelength beyond which an excitation photon cannot excite the transition associated with that absorption band.

[0153] Referring to FIG. 15, there is shown the energy levels of the rare-earth ion Er^{3+} in a KPb_2Cl_5 host crystal, to which the laser cooling method 200 may be applied. As can be seen from this diagram, the absorption spectrum of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ includes two absorption bands corresponding to the

$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ and $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transitions. The wavelengths corresponding to these transitions are 1530 nm and 810 nm, respectively.

[0154] Referring back to FIG. 14, the laser cooling method 200 next involves a step 204 of illuminating the sample of the fluorescent material with a first pump laser beam having a first pump wavelength that is longer than the corresponding maximum absorption wavelength of one of the at least one absorption band, so as to generate an anti-Stokes cooling cycle. As one skilled in the art will understand, the step 204 of illuminating the sample with the first pump laser consists in producing optical cooling is via a traditional anti-Stokes cooling cycle, the characteristics of which have been described above and shown, for example, in FIG. 2 (PRIOR ART).

[0155] In the embodiment shown in FIG. 15, the absorption band excited by the first pump laser beam corresponds to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$, which has maximum absorption wavelength equal to 1530 nm. Hence, according to the current method 200, a suitable wavelength $\lambda_p^{(1)}$ for the first pump laser beam may be $\lambda_p^{(1)}=1567\text{ nm}$, but may also have a different value, as long as $\lambda_p^{(1)}=1530\text{ nm}$.

[0156] Referring again to FIG. 14, the laser cooling method 200 involves, simultaneously to the previous step 202, a step 204 of illuminating the sample of the fluorescent material with a second pump laser beam having a second pump wavelength, the second pump wavelength being selected for exciting electrons of the fluorescent material so as to generate an upconversion cooling cycle. As a result, the anti-Stokes and the upconversion cooling cycles act cooperatively to induce a cooling of the sample of the fluorescent material.

[0157] As known in the art, the first and second pump laser beams according to the laser cooling method 200 may be produced by a laser source, which may be embodied, for example, by an electrically-pumped semiconductor lasers, an optically-pumped solid-state laser, an optical fiber laser, a solid state amplification system, an optical parametric amplification system, a fiber amplification system, a chirped pulse amplification system, a combination of these lasers and amplification systems, or the like.

[0158] As mentioned above, the upconversion cooling cycle according to this laser cooling method 200 may involve different mechanisms, including ESA, ETU, multiphoton absorption through virtual levels, or a combination thereof. Hence, it will be understood herein that the wavelength $\lambda_p^{(2)}$ of the second pump laser beam may, but need not, correspond to any absorption band of the fluorescent material and need not be able to excite an electron other than by a multiphoton absorption process.

[0159] In an embodiment of the invention, the laser cooling method 200 is performed on a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$, that is, by applying simultaneously thereto a traditional anti-Stokes cooling cycle and an upconversion cooling cycle. The $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ sample is considered to be pumped simultaneously at a first and a second pump wavelengths equal to $\lambda_p^{(1)}=1567\text{ nm}$ and $\lambda_p^{(2)}=860\text{ nm}$, as illustrated in FIG. 15. The first pump laser beam at a pump power value $P_p^{(1)}$ provides cooling via a traditional anti-Stokes cooling cycle, while the second pump laser beam at a pump power value $P_p^{(2)}$ provides cooling via an upconversion cooling cycle. Contrary to the case wherein $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ is cooled with the traditional cooling cycle alone, in the embodiment of FIG. 15, the $^4\text{I}_{13/2}$ is additionally populated with electrons which relax from higher lying levels (e.g. $^4\text{I}_{9/2}$, $^4\text{S}_{3/2}$, $^2\text{H}_{9/2}$).

[0160] Upconversion processes in Er^{3+} -doped KPb_2Cl_5 have been investigated in details by Galba et al. [see R. Balda et al., Phys. Rev. B vol. 69, p. 205203 (2004)]. As shown therein, the energy gap between the $^4\text{I}_{9/2}$ and $^4\text{I}_{11/2}$ levels in chloride systems is too large to be effectively bridged by multiphonon relaxation so that, in this case, the $^4\text{I}_{9/2}$ level acts as an intermediate level for upconversion processes, contrary to oxide and fluoride systems wherein excitation into the $^4\text{I}_{9/2}$ level is followed by fast non-radiative decay to the $^4\text{I}_{11/2}$ level due to the relatively high phonon energies.

[0161] Furthermore, it will be understood that the population dynamics of the electronic levels taking part in the simultaneous traditional and upconversion cooling cycles may be taken into account by the following set of rate equations:

$$\frac{dN_1}{dt} = \frac{I_p^{(1)}\lambda_p^{(1)}}{hc} [\sigma_a^{(1)}N_0 - \sigma_e^{(1)}N_1] - \frac{N_1}{\tau_1} + \beta_{21}\frac{N_2}{\tau_2} + \beta_{31}\frac{N_3}{\tau_3} + \beta_{41}\frac{N_4}{\tau_4} + \gamma_2N_2^2 - 2\gamma_1N_1^2, \quad (23)$$

$$\frac{dN_2}{dt} = \frac{I_p^{(2)}\lambda_p^{(2)}}{hc} [\sigma_a^{(2)}N_0 - \sigma_e^{(2)}N_2] - \beta_{20}\frac{N_2}{\tau_2} - \beta_{21}\frac{N_2}{\tau_2} - 2\gamma_2N_2^2 - \sigma_{ESA}^{(24)}\frac{I_p^{(2)}\lambda_p^{(2)}}{hc}N_2 + \gamma_1N_1^2 + \sigma_e^{(2)}\frac{I_p^{(2)}\lambda_p^{(2)}}{hc}N_4 - \sigma_{ESA}^{(23)}\frac{I_p^{(1)}\lambda_p^{(1)}}{hc}N_2,$$

$$\frac{dN_3}{dt} = -\beta_{30}\frac{N_3}{\tau_3} - \beta_{31}\frac{N_3}{\tau_3} + \gamma_2N_2^2 + \sigma_{ESA}^{(23)}\frac{I_p^{(1)}\lambda_p^{(1)}}{hc}N_2,$$

$$\frac{dN_4}{dt} = \frac{I_p^{(2)}\lambda_p^{(2)}}{hc} [\sigma_{ESA}^{(24)}N_2 - \sigma_e^{(2)}N_4] - \beta_{40}\frac{N_4}{\tau_4} - \beta_{41}\frac{N_4}{\tau_4},$$

with

$$N_T = N_0 + N_1 + N_2 + N_3 + N_4, \quad (24)$$

where N_i ($i=0, \dots, 4$) and τ_i are respectively the population and radiative lifetime of the i^{th} level, N_T is the total density of active ions in the sample, while β_{i0} and β_{i1} are respectively the branching ratios for the i to 0 and i to 1 transition. Moreover, γ_1 is the strength of the ETU process, by which one electron in level $^4\text{I}_{13/2}$ decays to the $^4\text{I}_{15/2}$ and, at the same time, another electron in a different ion is promoted from the $^4\text{I}_{13/2}$ level to the $^4\text{I}_{9/2}$ energy level. Likewise, γ_2 is the strength of the ETU process in which one electron in level $^4\text{I}_{9/2}$ decays to the $^4\text{I}_{13/2}$ and, at the same time, another electron in a different ion is promoted from the $^4\text{I}_{9/2}$ level to the $^4\text{S}_{3/2}$ energy level. Finally, $\sigma_{ESA}^{(23)}$ is the ESA cross-section at the pump wavelength $\lambda_p^{(1)}$, $\sigma_{ESA}^{(24)}$ is the ESA cross-section at the pump wavelength $\lambda_p^{(2)}$, and $I_p^{(1)}$ and $I_p^{(2)}$ are the pump intensities at the wavelengths $\lambda_p^{(1)}$ and $\lambda_p^{(2)}$, respectively.

[0162] In the general case, the system of Equation (24) cannot be solved analytically. However, analytical approximations may be used to find a solution to the system is under the reasonable approximations that the radiative components are much larger than the other terms that depopulate the level. This condition may be expressed mathematically by the following inequalities:

$$\frac{N_1}{\tau_1}, \frac{N_2}{\tau_2}, \frac{N_3}{\tau_3} \gg \gamma_1N_1^2, \gamma_2N_2^2 \quad (25)$$

[0163] At steady-state, the populations of the levels satisfies the relation $dN_i/dt=0$, with $i=0, \dots, 4$. As a result, the net cooling power deposited into the sample may be expressed as

$$P_{cool} = -A_{eff}L[I_p^{(1)}[\sigma_a^{(1)}N_0 - \sigma_e^{(1)}N_1] + I_p^{(2)}[\sigma_a^{(2)}N_0 - \sigma_e^{(2)}N_2 + \sigma_{ESA}^{(24)}N_2 - \sigma_e^{(2)}N_4]] + A_{eff}Lhc\left(\frac{N_1}{\tau_1\tilde{\lambda}_1} + \beta_{20}\frac{N_2}{\tau_2\tilde{\lambda}_{20}} + \beta_{21}\frac{N_2}{\tau_2\tilde{\lambda}_{21}} + \beta_{30}\frac{N_3}{\tau_3\tilde{\lambda}_{30}} + \beta_{31}\frac{N_3}{\tau_3\tilde{\lambda}_{31}} + \beta_{40}\frac{N_4}{\tau_4\tilde{\lambda}_{40}} + \beta_{41}\frac{N_4}{\tau_4\tilde{\lambda}_{41}}\right) + \alpha_bI \quad (26)$$

where α_b is the background absorption coefficient and $A\tilde{\lambda}_{ij}$ is the mean fluorescence wavelength for the $i \rightarrow j$ transition. Using Equation (26), it may be possible to calculate the net cooling power deposited into the sample as function of the pump power of the first and second pump laser beams at wavelengths $\lambda_p^{(1)}$ and $\lambda_p^{(2)}$, respectively.

[0164] In an embodiment of the laser cooling method 200 according to an aspect of the invention, a cylindrical sample of a KPb_2Cl_5 host material doped with Er^{3+} is pumped simultaneously with a first and a second pump laser beams at wavelengths $\lambda_p^{(1)}=1567$ nm and $\lambda_p^{(2)}=860$ nm. The first pump laser beam provides cooling with a traditional anti-Stokes cooling cycle that involves the $^4\text{I}_{15/2}$ and $^4\text{I}_{13/2}$ levels. One skilled in the art will recognize that this is the same transition used in optical communications is in the 1500 nm window, so that lasers at this frequency are well developed. The second pump source provides cooling based on an upconversion cycle, which includes the $^4\text{I}_{15/2}$, $^4\text{I}_{9/2}$ and $^2\text{H}_{9/2}$ levels.

[0165] Referring to Equation (5), in some embodiments of the laser cooling method 200, the values of the first and second pump wavelengths $\lambda_p^{(1)}$ and $\lambda_p^{(2)}$ are preferably selected so as to yield pump photon energies $E_p^{(1)}=hc/\lambda_p^{(1)}$ and $E_p^{(2)}=hc/\lambda_p^{(2)}$ equal to at least eight times a maximum phonon energy $\hbar\omega_{max}$ of the host material.

[0166] To perform the simulations presented below in FIGS. 16 and 17, the spectroscopic properties of Er^{3+} : KPb_2Cl_5 crystals were used based on investigations performed by other workers in the field [see, R. Balda et al., Phys. Rev. B vol. 69, p. 205203 (2004), Z. Hasan et al., Proc. SPIE vol. 7228, p. 72280H (2009) and A. Ferrier et al., J. Opt. Soc. Am. B vol. 24, p. 2526 (2007)]. The absorption spectra for the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ and $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transitions are illustrated in K. Nitsch et al., J. Cryst. Growth vol. 131, p. 612 (1993) (see, respectively, FIGS. 6 and 3 therein), while the excited-state absorption cross section for the $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$ transition is illustrated in A. Ferrier et al., J. Opt. Soc. Am. B vol. 24, p. 2526 (2007) (see FIG. 7 therein).

[0167] In particular, Ferrier et al. that the ESA cross section for the $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$ transition is comparable to the ground-state absorption cross section of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition. As a result, one skilled in the art will understand that this means that upconversion plays a significant role in this optical cooling process. Moreover, it was shown by Z. Hasan et al. that the absorption strength of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition is much weaker than that of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition. Hence, by taking into account the extremely weak absorption for the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition, one skilled in the art may understand why the temperature of the sample dropped by 0.7 ± 0.1 K, thus resulting in an upconversion-based cooling cycle with a very low cooling efficiency.

[0168] On the contrary, in the laser cooling method **200** described herein, the $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ sample is pumped simultaneously with two pump laser beams so as to produce a traditional anti-Stokes cooling cycle and an upconversion cooling cycle that act cooperatively to induce a cooling of the sample. Using Equation (26), it is possible to calculate the net cooling power P_{cool} deposited in the sample as a function of the pump powers $P_p^{(1)}$ and $P_p^{(2)}$ of the first and second pump laser beams, respectively. In the simulations presented in FIGS. 16 and 17, the diameter and length of the cylindrical sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ are $D=3$ mm and $L=3$ mm.

[0169] In general, the process of fluorescence re-absorption and trapping in solid-state optical materials may influence the efficiency of optical cooling. However, it was shown that the effect of radiation trapping may be neglected in this range of diameters [see N.J. Condon et al., Opt. Express vol. 17, p. 5466 (2009)]. Moreover, it was estimated that the depletion of the pump power over the length of the sample is insignificant so that it was not taken into account in the simulations.

[0170] Referring now to FIG. 16, there is shown a graph of the net cooling power P_{cool} of a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ as a function of the pump power $P_p^{(1)}$ of the first pump laser beam, at a wavelength $\lambda_p^{(1)}=1567$ nm, for different values of the second pump power $P_p^{(2)}$ of the second pump laser beam, at a wavelength $\lambda_p^{(2)}=860$ nm, according to an embodiment of the laser cooling method **200**. Upon examination of FIG. 16, it may be concluded that adding the second pump laser beam with pump power $P_p^{(2)}$ may increase the net cooling power P_{cool} deposited into the sample, even though the cooling efficiency provided by $P_p^{(2)}$ at $\lambda_p^{(2)}=860$ nm is relatively weak. Indeed, a pump power $P_p^{(2)}=2$ kW should be provided in order to increase the net cooling power P_{cool} deposited into the sample by about 0.45 μW .

[0171] In some embodiments of the laser cooling method **200**, the sample may be mounted in a vacuum chamber, so that only radiative heat load takes place. In these embodiments, supplementing a pump power $P_p^{(2)}\approx 2$ kW via the second pump laser beam at $\lambda_p^{(2)}=860$ nm may provide an additional 100 K drop in the temperature of the sample.

[0172] Referring now to FIG. 17, there is shown a graph illustrating the net cooling power P_{cool} of a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ as a function of the pump power $P_p^{(2)}$ of the second pump laser beam, at a wavelength $\lambda_p^{(2)}=860$ nm, for different values of the first pump power $P_p^{(1)}$ of the first pump laser beam, at a wavelength $\lambda_p^{(1)}=1567$ nm, according to an embodiment of the invention. Upon examining FIG. 17, it can be seen that when the value of the pump power $P_p^{(1)}$ at $\lambda_p^{(1)}=1567$ nm is zero, the net cooling power P_{cool} deposited in the sample is only 0.45 μW , even with a very high pump power of $P_p^{(2)}=2$ kW.

[0173] However, as can be seen from FIG. 17, even a small amount of supplementary pump power $P_p^{(1)}$ at $\lambda_p^{(1)}=1567$ nm applied to the sample significantly affects the value of cooling power P_{cool} deposited into the sample and proves that the laser cooling method **200** according to an aspect of the invention and based on a combination of a traditional anti-Stokes cooling cycle and an upconversion cooling cycle may be more is than a cooling cycle based only upconversion. Indeed, the supplementary pump power $P_p^{(1)}=25$ W at $\lambda_p^{(1)}=1567$ nm increases the net cooling power deposited in the sample by 1.9 μW . Furthermore, in embodiments of the method **200** wherein the sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ is mounted in a vacuum chamber, the supplementary pump power $P_p^{(1)}$ may provide an additional 180 K drop in the temperature of the sample.

[0174] As one skilled in the art will readily understand, broadened spectral absorption lines at or near room temperature become significantly narrower and more intense as temperature is lowered. As the sample cools, the thermal population of those lines decreases, such that cooling slows and eventually stops. Moreover, laser cooling is generally sensitive to impurities, for example hydroxyl ions OH^- or microscopic defects in glasses. Indeed, impurities open up various pathways for the excitation to decay by non-radiative relaxation, which thereby cause what can be referred to as “parasitic heating”.

[0175] In summary, the laser cooling process of a sample of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ pumped simultaneously with two pump laser beams at wavelengths of 860 nm and 1567 nm has been presented as an exemplary embodiment of the laser cooling method **200** according to an aspect of the invention. It was shown that simultaneous pumping of the $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ sample at two wavelengths leads to an increase in the net cooling power deposited into the sample due to a combination of a traditional anti-Stokes cooling cycle and an upconversion cooling cycle, wherein the two cooling cycles act cooperatively to help to overcome the self-termination effects that may present in either of the two cooling cycles when used on its own.

[0176] Of course, numerous modifications could be made to the embodiments described is above without departing from the scope of the present invention.

1. A method for cooling a fluorescent material, the method comprising the steps of:

- a) providing a sample of the fluorescent material, the sample having an elongated light propagation direction, the fluorescent material exhibiting fluorescence at a mean fluorescence wavelength and being capable of entering a superradiance regime wherein superradiant pulses are emitted with a formation delay time;
- b) generating a pump laser beam comprising laser pulses, the generating comprising the substeps of:
 - i) selecting a pump wavelength of the pump laser beam that is longer than the mean fluorescence wavelength of the fluorescent material;
 - ii) selecting a pump power of the pump laser beam so as to reach the superradiance regime of the fluorescent material; and
 - iii) selecting a pulse duration of the laser pulses that is shorter than the is formation delay time of the superradiant pulses; and
- c) directing the laser pulses of the pump laser beam onto the sample of the fluorescent material along the elongated light propagation direction thereof so as to produce the superradiant pulses in an anti-Stokes process inducing a cooling of the sample.

2. The method according to claim 1, comprising a step of mounting the sample of the fluorescent material in a vacuum chamber prior to directing the laser pulses thereonto.

3. The method according to claim 1, wherein the fluorescent material is a solid material comprising a host material doped with ions of a rare-earth element.

4. The method according to claim 3, wherein the host material is one of a glass and a crystal.

5. The method according to claim 4, wherein the host material is selected from the group consisting of a fluoride glass, a fluoro-chloride glass, an oxide crystal, a fluoride crystal and a chloride crystal.

6. The method according to claim 3, wherein the rare-earth element is selected from the group consisting of ytterbium, thulium and erbium.

7. The method according to claim 1, wherein the sample of the fluorescent material is shaped as a cylinder.

8. The method according to claim 1, wherein the sample of the fluorescent material is shaped as a rectangular parallelepiped.

9. The method according to claim 1, wherein the sample of the fluorescent material is a sphere supporting whispering-gallery modes.

10. The method according to claim 3, further comprising adjusting a temperature of the sample of the solid material so as to adjust a threshold value for a number of excited ions in the host material beyond which the solid material enters in the superradiance regime.

11. A method for cooling a fluorescent material, the method comprising the steps of:

- a) providing a sample of the fluorescent material, the fluorescent material having an absorption spectrum comprising at least one absorption band, each of the at least one absorption band having a corresponding maximum absorption wavelength;
- b) illuminating the sample of the fluorescent material with a first pump laser beam having a first pump wavelength that is longer than the corresponding maximum absorption wavelength of one of the at least one absorption band, so as to generate an anti-Stokes cooling cycle; and, simultaneously,
- c) illuminating the sample of the fluorescent material with a second pump laser beam having a second pump wavelength, the second pump wavelength being selected for exciting electrons of the fluorescent material so as to generate an upconversion cooling cycle,

wherein the anti-Stokes and the upconversion cooling cycles act cooperatively to induce a cooling of the sample of the fluorescent material.

12. The method according to claim 11, comprising a step of mounting the sample of the fluorescent material in a vacuum chamber prior to steps b) and c).

13. The method according to claim 11, wherein the fluorescent material is a solid material comprising a host material doped with ions of a rare-earth element.

14. The method according to claim 13, wherein the host material is one of a glass and a crystal.

15. The method according to claim 14, wherein the host material is selected from the group consisting of a fluoride glass, a fluoro-chloride glass, an oxide crystal, a fluoride crystal and a chloride crystal.

16. The method according to claim 13, wherein the rare-earth element is selected from the group consisting of ytterbium, thulium and erbium.

17. The method according to claim 11, wherein the upconversion cooling cycle comprises an excited state absorption process and a cooperative energy-transfer upconversion process.

18. The method according to claim 13, wherein the solid material is a potassium-lead chloride crystal doped with trivalent erbium ions.

19. The method according to claim 18, wherein the first pump wavelength is selected so that the anti-Stokes cooling cycle comprises $^4I_{15/2}$ and $^4I_{13/2}$ absorption bands of the potassium-lead chloride crystal doped with erbium, and wherein the second pump wavelength is selected so that the upconversion cooling cycle comprises $^4I_{15/2}$, $^4I_{13/2}$ and $^4H_{9/2}$ absorption bands.

20. The method according to claim 19 wherein the first and second pump wavelengths are equal to about 1567 and 860 nanometers, respectively.

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