optica

Conservation of photon rate in endothermic photoluminescence and its transition to thermal emission

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Received 6 April 2015; revised 20 May 2015; accepted 27 May 2015 (Doc. ID 237558); published 19 June 2015

Photoluminescence (PL) is a fundamental light–matter interaction that conventionally involves the absorption of an energetic photon, thermalization, and the emission of a redshifted photon. Conversely, in optical refrigeration, the absorption of a low-energy photon is followed by endothermic PL of an energetic photon. These two quantum processes are, in contrast to thermal emission, governed by photon-rate conservation. Thus far, both aspects of PL have been studied under thermal population that is far weaker than the photonic excitation, hiding the role of rate conservation when thermal excitation is significant. Here we theoretically and experimentally study endothermic PL at high temperatures. In contrast to thermal emission, we find that the PL photon rate is conserved with temperature increase, while each photon is blueshifted. Further rise in temperature leads to an abrupt transition to thermal emission where the photon rate increases sharply. We also demonstrate how endothermic PL generates orders of magnitude more energetic photons than thermal emission at similar temperatures. These new findings show that endothermic PL is an ideal optical heat pump. This opens the way for a proposed novel device that harvests thermal losses in photovoltaics with record efficiency. © 2015 Optical Society of America

OCIS codes: (250.5230) Photoluminescence; (160.2540) Fluorescent and luminescent materials; (160.6840) Thermo-optical materials; (040.5350) Photovoltaic.

http://dx.doi.org/10.1364/OPTICA.2.000585

Photoluminescence (PL) is a quantum process governed by conservation of photon rate [1]. In optical refrigeration, endothermic PL is generated by a narrow-line pump at the absorption tail of a photoluminescent material, followed by emission at shorter wavelengths [2,3]. Recent studies have demonstrated cryogenic temperatures with doped glasses of quantum efficiency (QE) approaching unity [4]. Thus far, endothermic PL has been studied under thermal population that is far weaker than the photonic excitation. Under this condition, the photon rate conservation of the PL process is undisturbed by the thermal emission, obscuring the generalization of PL and thermal emissions. In this Letter we theoretically and experimentally study endothermic PL at high temperatures, where thermal and PL excitations compete in populating states above the bandgap. The fundamental physics that governs the interplay between PL and thermal emissions is expressed by the generalized Planck law, describing the spontaneous emission rate of a photoluminescent material [1,5] (similar formulations for the spontaneous emission rate of luminescent systems can be found in Refs. [6–11]):

$$R(\hbar\omega, T, \mu) = \varepsilon(\hbar\omega) \cdot \frac{(\hbar\omega)^2}{4\pi^2\hbar^3c^2} \frac{1}{e^{\frac{\hbar\omega-\mu}{K_B T}} - 1} \cong R_0 \cdot e^{\frac{\mu}{K_B T}}, \quad (1)$$

where R is the emitted photon flux (photons per second per unit area). Here, T is the temperature, ε is the emissivity, $\hbar\omega$ is the photon energy, K_b is Boltzmann's constant, and μ is the chemical potential. The corresponding emitted energy rate is defined by $E(\hbar\omega, T, \mu) = R(\hbar\omega, T, \mu) \cdot \hbar\omega$. The chemical potential $\mu > 0$ defines the level of excitation above the system's thermal equilibrium, and is frequency-invariant at the spectral band wherein thermalization equalizes excitation levels between modes. This is true for excited electrons in the conduction band of solid-state semiconductors, as well as for excited electrons in isolated molecules [1]. By its definition, for a fixed excitation rate, as thermal excitation increases, μ is reduced, and when $\mu = 0$ the radiation is reduced to thermal emission. Thermodynamically, the chemical potential is defined as long as the number of particles is conserved, which for PL means constant QE, i.e., the ratio between the emitted and absorbed photon rates. Equation (1) describes the excitation of electrons at a specific band where μ is constant. Although this theoretical formalism and the thermodynamics of optical refrigeration [12,13] are well established, the regime where thermal excitation is comparable to the level of photonic excitation has not yet been explored. We start by noticing that any additional thermal excitation of electrons from the ground state, i.e., thermal emission that rapidly grows with the rise of temperature, cannot be added to the PL rate described by Eq. (1). This is because such a sum of emissions would result in total thermal emission (at $\mu = 0$) that exceeds the blackbody radiation.

With this in mind, our research hypothesis is that, under a steady PL pump, and as long as $\mu > 0$, the PL emission rate is constant regardless of temperature. This is true as long as the QE is not affected by temperature. For such a PL system, both energy and rate conservation between the absorbed and the emitted radiation fluxes must be satisfied. The fixation of photon rate leaves only the photon energy as a degree of freedom for a change in the system's total energy. For this reason, increasing the heat flux absorbed in the system while the PL pump rate is constant must result in temperature rise and a blueshift in the PL spectrum. Another part of the hypothesis is that such endothermic PL is a very efficient heat pump that enhances the emission rate of energetic photons above the thermal radiation limit.

We start with simulating the PL evolution of an ideal material, under constant optical pump rate and temperature increase. Physically, as will be shown, this corresponds to a situation where the material is optically pumped at its absorption resonance, generating constant PL, with additional variable heat flux that controls the temperature. For the sake of generality, the material is chosen to have a band-like emissivity function, as shown in Fig. 1(a) (inset). This emissivity function can describe both materials with discrete energy gaps, such as small molecules, and semiconductors (by expending the emissivity into the high energy spectrum). As an example, the emissivity function is chosen to be unity between 1.3 and 1.7 eV and zero elsewhere. In addition, for simplicity the PL is assumed to have unity QE and only radiative heat transfer is accounted for. In line with our hypothesis, we solve Eq. (1) by balancing the incoming and outgoing photonic and energy rates, at steady state. For a given incoming photon and energy rate the solution uniquely defines the thermodynamic state of the PL absorber, which is characterized by its quantities T and μ. The only way to conserve both the PL and energy rates is if each emitted photon is blueshifted with the increase in pumped heat. Figure 1(a) presents the evolution of emission spectrum and chemical potential (inset) as a function of temperature. Figure 1(b) presents the total emitted photon rate (inset) and the rate of photons with energy above 1.45 eV in the case of endothermic PL (blue line) and thermal emission (red line). The thermal emission is calculated by setting $\mu = 0$, and applying only the energy balance. As evident, at low temperatures, the emission's line shape at the band edge is narrow, and is blueshifted with temperature increase [Fig. 1(a)], while the total emitted photon rate is conserved [Fig. 1(b) inset]. Remarkably, this process is characterized by the reduction of photon rate near the band edge, where electrons are being thermally pumped to the high-energy regime as long as $\mu > 0$. The red portion of the emission in Fig. 1(a) represents the thermal population, R_0. At low temperatures the PL photon rate is far above the rate of thermal emission, while R_0 increases and becomes significant at high temperatures. The temperature rise leads to the reduction in the chemical potential, according to the relation

$$\mu(T) = K_B T \cdot \ln\left(\frac{\int R \cdot \mathrm{d}(\hbar\omega)}{\int R_0 \cdot \mathrm{d}(\hbar\omega)}\right), \tag{2}$$

where R is the total PL rate in the specific band and R_0 is the total thermal emission rate in the band. This trend continues until $\mu = 0$, where the emission becomes purely thermal. For the computation in this case the constraint for balance between the absorbed and PL photon rates is removed. Further rise in temperature results in a sharp increase of the photon rate at all wavelengths. Examining the generation rate of photons with energy above 1.45 eV, corresponding to $\lambda < 850$ nm [Fig. 1(b)] shows that the emitted rate of energetic photons in the endothermic PL case (blue line) is orders of magnitude greater than in thermal emission under the same temperatures (red line). Also for the energetic photon rate, at $\mu = 0$, the two emissions converge.

Moving to the experimental part, the need for high-QE PL at high temperatures limits the use of solid-state semiconductors, due to reduction in their QE by temperature-dependent nonradiative recombination mechanisms [14]. On the other hand, rare-earth ions such as neodymium and ytterbium are an excellent choice of materials as their electrons are localized and insulated from interactions. This results in the conservation of their high QE at extremely high temperatures [15]. Due to the lack of interaction between electrons, each energy gap can be populated at different μ values, but thermalization equalizes μ within each spectral band. We experimentally study the transition between the PL and thermal emission at the 905 nm fluorescence band of a neodymium (Nd^{+3})-doped silica fiber tip under 532 nm PL excitation of a few milliwatts (mW). The 905 nm emission corresponds to the transition between the $4F_{3/2}$ and $4I_{9/2}$ energy levels of the Nd^{3+} system, the latter being the ground state, which is essential for maximizing the thermal radiation signal. To control the heat load separately from the PL excitation, we use a CO_2 laser operating at 10.6 μm wavelength with power levels up to 150 mW. At this wavelength, the photons are efficiently absorbed

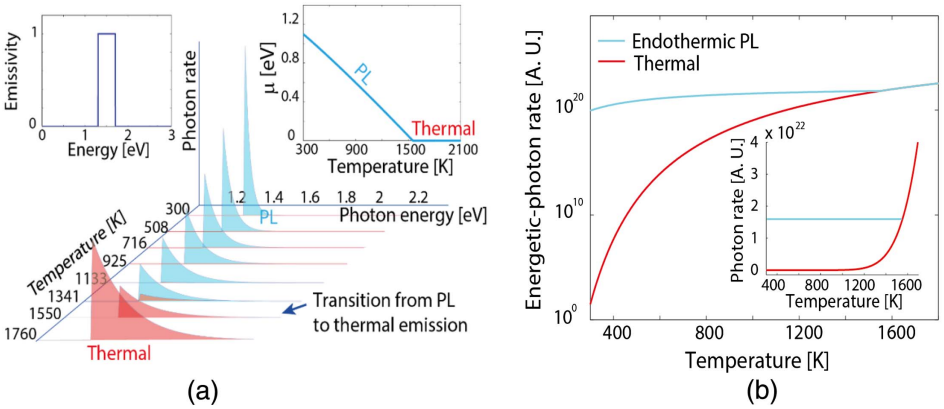

Fig. 1. (a) Emission evolution of PL material with temperature. Insets: the emissivity function and the chemical potential temperature dependence. (b) Emission rates of energetic photons and total photon rate (inset) for PL (blue line) and thermal emission (red line) at various temperatures.

by the silica matrix [16] and converted to a constant heat flow. Although the 532 nm pump is exothermic in the sense that the absorbed energy is higher than the emitted PL energy, the heat associated with the few-mW pump thermalization is negligible, in comparison with the heat load imposed by the CO_2 laser. Therefore, the PL harvests the thermal energy pumped by the CO_2 laser, and, thus, it is endothermic. The temperature and the chemical potential are uniquely defined by these two pumps. The experimental setup is sketched in Fig. 2(a). The power spectrum is measured by a calibrated spectrometer. The weak PL excitation at 532 nm is kept constant at 1 mW, while the CO_2 laser power varies between 0 and 150 mW. We monitor the temperature by fluorescence intensity ratio thermometry [17] (see Supplement 1). The spectral results are shown in Fig. 2(b). As we increase the thermal load, the temperature rises, and the PL exhibits a blueshift evolution. This is shown by the reduction in the emission of the low photon-energy peak at 905 nm, and enhancement of the high photon-energy peak at 820 nm. This trend continues until it reaches the transition temperature of ~1500 K. As we increase the temperature further, the emitted photon rate increases sharply at all wavelengths [dotted lines in Fig. 2(b)]. Figure 2(c) shows the total number of emitted photons at wavelengths between 600 and 1000 nm (blue line). To compare PL to thermal emission under equivalent conditions, we turn off the weak PL pump while the thermal current is unchanged (red line). The thermal emission at temperatures lower than 1150 K is below our detection limit and we extrapolate the experimental values down to 300 K. The inset of Fig. 2(c) shows that the measured chemical potential values (blue dots) are in good agreement with the theory (gray line) (see detailed description in Supplement 1). As demonstrated, the total photon rate is conserved at various temperatures, as long as $\mu > 0$, and increases sharply at $\mu = 0$, while converging with the thermal emission.

In Fig. 2(d) we compare the emission rate of energetic photons at wavelengths between 600 and 850 nm under PL excitation of 1 mW (blue line) and 4 mW (purple line) to thermal emission (red line). As can be seen, at temperatures below 1300 K the energetic-photon rates generated by endothermic PL excitation exceed that of thermal emission at similar temperatures by orders of magnitude.

The experimental part clearly validates our hypothesis on the nature of PL rate conservation with temperature rise. This can be simply seen by the convergence of the PL and thermal lines in Fig. 2(c): if the photon conservation law is not applied, the two separated curves could not converge. Also in Fig. 2(d), the order of magnitude enhancement in energetic photons emitted by endothermic PL between 400 and 1100 K (blue and purple curves) cannot be explained by the contribution of thermal emission (red curve). Last, in agreement with our theoretical model, the reduction of the low-energy PL photon rate (near 905 nm), is completely compensated by the increase of PL photon rate at 820 nm. Therefore, we demonstrated enhanced spectral blueshift, which is the outcome of energy balance in a number-conserved photonic system.

Another discussion should be addressed to the experimental evolution of endothermic PL near the critical temperature where the transition from PL to thermal emission is abrupt but not as sharp as expected from the simulation. We note that for PL, photons are pumped at a certain energy and emitted at a different one, which requires directional energy transfer. This is in contrast to the meaning of complete thermal equilibrium between modes through thermalization. In other words, thermalization only

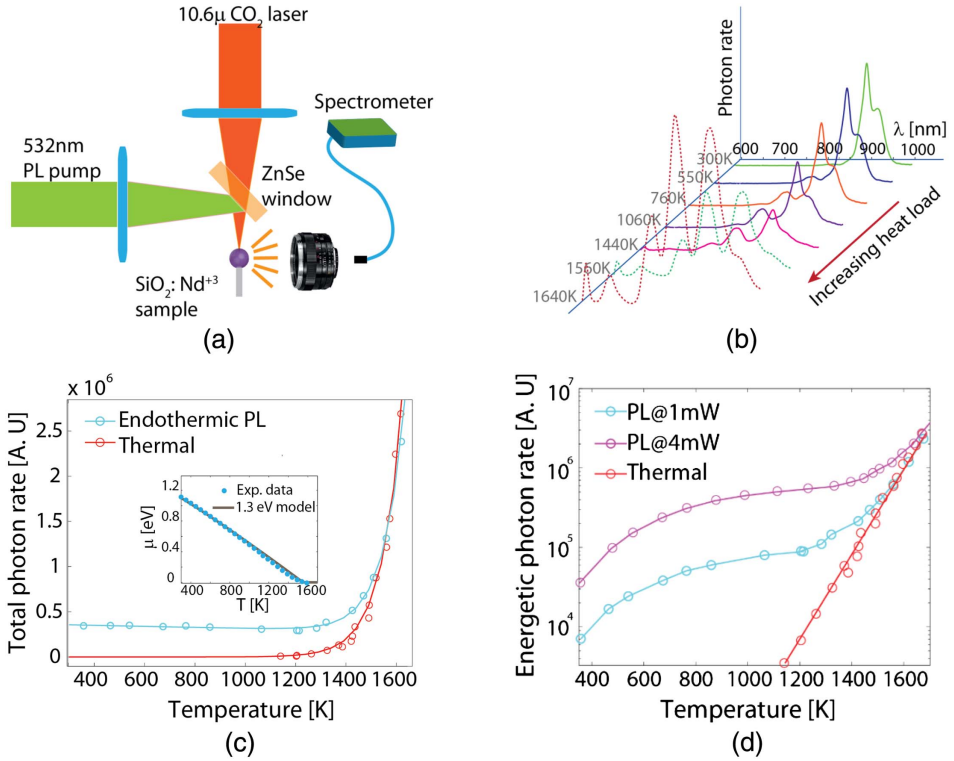

Fig. 2. (a) Experimental setup. (b) PL spectra evolution with temperature. (c) Total photon rate of PL and thermal emissions (inset: chemical potential versus temperature). (d) Energetic photon ($\lambda < 850$ nm) rate for PL and thermal emissions.

approximately equilibrates between adjacent frequencies, and small variation in the chemical potential is inevitable. We postulate that at the critical temperature these small differences in chemical potential lead to gradual transition into thermal emission. Other smearing effects of the transition could be unequal distribution of excitation and temperature across the sample.

Before concluding, we note that such a "thermally enhanced PL" (TEPL) can be used as an efficient heat pump. This can be considered for conversion of heat to electricity in a similar way to the solar thermal photovoltaics (STPV) concept [18,19], in which the energetic portion of thermal radiation is harvested by a low bandgap photovoltaic cell. While STPV efficiency depends on the thermal radiation, R_0, TEPL efficiency depends on the enhanced emission R. This advantage is related to the reduced entropy in TEPL in comparison with STPV when emitting the same energy flux. While a thermal emitter is always characterized by maximal entropy per energy, the TEPL is characterized by reduced entropy due to $\mu > 0$. This can be seen from the entropy term in the Gibbs free energy equation:

$$S_{\mathrm{TEPL}} = \frac{E - \mu N}{T} = S_{\mathrm{thermal}} - \frac{\mu N}{T}, \tag{3}$$

where S_{thermal} is the entropy of a thermal emitter with the same total energy E. A specific example for such a converter can be a solar-energy-based TEPL device, wherein the incoming solar flux is absorbed by a low bandgap PL material. In addition to the PL excitation, the otherwise lost thermalization heat raises the temperature and allows the TEPL emission to be coupled to a higher bandgap solar cell. The excessive thermal energy is then converted to electrical work at high voltage and enhanced efficiency. Recent results show that a TEPL-based device can reach theoretical maximal efficiencies of 70%, as high as in STPV. More importantly, while the operating temperature of STPV is of the order of 2000°C, the TEPL operation temperature is below 1000°C [20].

To conclude, we theoretically and experimentally study endothermic PL at high temperatures. Our findings demonstrate how endothermic PL, in contrast to thermal emission, conserves the photon rate while the emission is blueshifted due to temperature rise. We also demonstrate how, at a critical temperature, the PL abruptly transforms into thermal emission where the photon rate increases sharply with temperature. Finally, we demonstrate how such a number-conserved photonic system is more efficient in emitting energetic photons than thermal radiation. These new findings show that endothermic PL is an ideal optical heat pump. We envision a novel TEPL-based device that harvests thermal losses in photovoltaics with record efficiency.

Russell Berrie Nanotechnology Institute (RBNI); Grand Technion Energy Program (GTEP); Leona M. and Harry B. Helmsley Charitable Trust reports on Alternative Energy series of the Technion and the Weizmann Institute of Science (2012PG-ISL003); Focal Technology Area on Nanophotonics for Detection.

The authors would like to acknowledge Prof. Peter Würfel and Prof. Eli Yablonovitch for their support and valuable insights. We would also like to thank Asst. Prof. Avi Niv for the constructive brainstorming and Dr. Alexander Bekker for the help with sample fabrication. A. Manor thanks the Adams Fellowship program for financial support. C. Rotschild acknowledges the support of the Marie Curie International Reintegration Grant.

See Supplement 1 for supporting content.

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