Hot Brownian thermometry and cavity-enhanced harmonic generation with nonlinear optical nanowires

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Abstract

The non-linear response of nanoscale materials is affected by phase-matching conditions that are critically dependent on temperature. It has remained a persistent challenge to measure the temperature of individual nonlinear optical nanostructures in situ. Here, we measure the temperature of individual KNbO₃ nanowires in an optical trap through analysis of the Brownian dynamics. Additionally, we show Fabry-Pérot-type cavity enhancement of second harmonic generation in one-dimensional potassium niobate nanowires (KNNW) using a tunable, continuous wave (CW), near-infrared (NIR) trapping laser. A second co-aligned CW NIR laser is used to extend the range of visible emission through sum frequency generation.

Keywords: optical trap, potassium niobate, nonlinear, second harmonic, sum frequency, Brownian motion

Introduction

The nonlinear response of materials to intense electric fields were only realized after the advent of the laser. The first reported example was second harmonic generation (SHG) of a ruby laser in crystalline quartz [1]. Since then

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5 researchers in the field of nonlinear optics have demonstrated harmonics as high
as $n = 221$ [2]. Harmonic generation has a significant utility in converting lasers
beams of frequency ω into beams with frequency of $n\omega$ where n is an integer.
Other commonly used nonlinear effects include parametric processes such as sum
frequency generation (SFG), difference frequency generation (DFG), and opti-
10 cal parametric oscillation (OPO), or non-parametric processes like two-photon
absorption (TPA) and stimulated Raman scattering [3]. Applications of non-
linear processes vary significantly and include laser frequency modulation [1, 4],
two-photon luminescence [5], vibrational spectroscopy [6], two-photon medical
imaging [7], nonlinear photodynamic therapy [8, 9], and information technology
15 [10].

Nanostructures have gained in popularity as nonlinear optical materials
[11, 12, 13, 14, 15], notably for biomedical theranostics [16]. Applications include
drug delivery [17], photothermal [18] and photodynamic [19, 20] therapy, and
imaging [21]. Nonlinear nanoparticles are especially advantageous for biomed-
20 ical imaging [22] as they allow for the use of near infrared (NIR) light which
penetrates deeper into living tissue than visible light due to lower absorption
[23]. One-dimensional structures have the advantage of a large surface area pro-
viding a scaffold for adsorption and conjugation. Potassium niobate is a popular
nonlinear material [24] and has even had nonlinear effects demonstrated from
25 optically trapped nanowires [25]. However, knowing the temperature of KNbO_3
nanomaterials under NIR illumination is important not only for phase-matching
conditions but also if it is to be used in vivo for theranostic applications given the
low temperature threshold ($\sim 42^\circ\text{C}$ [26]) for cellular damage. Here, the Brow-
nian dynamics of optically trapped KNNWs are analyzed in order to extract
30 temperatures. Nonlinear processes, including SHG and SFG, are observed from
the trapped KNNWs and Fabry-Pérot type cavity enhanced SHG is demon-
strated using a tunable NIR laser which suggests the possibility of synthetically
tuning the lengths and diameters of nanowire cavities for increased harmonic
conversion [12, 13, 14].

Experimental

Monoclinic KNbO_3 nanowires were grown hydrothermally using a previously-reported method [27]. Briefly, 12.6 g of KOH was dissolved in 15 mL DI H_2O and sonicated for 5 minutes. After adding 0.87 g of niobium metal powder to this solution it was placed into a teflon-lined autoclave and heated to 150°C for 15 hours.

Samples for scanning electron microscopy (SEM), x-ray diffraction (XRD), and Raman spectroscopy were prepared by evaporating an aqueous suspension onto a clean silicon wafer. Scanning electron micrographs were acquired on a JEOL JSM-7000F scanning electron microscope in secondary electron imaging mode with a 10.0 kV accelerating voltage and 10.0 mm working distance. Bright field and select area electron diffraction (SAED) images were taken on a FEI Tecnai G2 F20 at an accelerating voltage of 200 keV. SAED images were taken with a camera length of 490 mm. XRD measurements were performed on a Bruker D8 Discover with GADDS XRD system using Cu K_α radiation. Raman spectra were obtained using a home-built setup using a Coherent Compass 532 nm SLM laser at 10 mW power. The laser was focused onto the sample using a Mitutoyo 50x long working distance objective ($\text{NA}=0.55$). Backscattered light was dispersed onto a Princeton liquid nitrogen-cooled silicon CCD using an Acton 500i SpectraPro spectrograph.

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy was performed on the Advance Light Source beamline 5.3.2.2 at Lawrence Berkeley National Laboratory. Samples were prepared by evaporating a $2\mu\text{L}$ suspension of nanowires onto a lacey carbon TEM grid and placing the TEM in the beamline under 0.33 atmospheres of helium. Soft x-rays (250 - 800 eV) were focused onto the sample with a spot size of 31 nm using 25 nm Fresnel zone plates. The oxygen K-edge was observed in the energy window of 525 - 550 eV.

Optical trapping of individual KNNWs was accomplished with a home-built system (Fig. 3). A 330 mW Thorlabs 975 nm diode laser, 4 W SpectraPhysics 1064 nm DPSS laser, and 10 W Sahajanad Laser Technology 1020-1040 nm

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65 tunable DPSS Yb:YAG disk laser were co-aligned, expanded, and focused into
10 a chamber using a Nikon 100x oil immersion objective (NA=1.25). SHG and
11 SFG signals were collected using the same objective and detected with the same
12 spectrometer used for the Raman measurements. Trapping chambers consisted
13 of 75x25x1 mm glass slide and #1 coverslip with a droplet of NW suspension
14 and imaging spacer (Grace Bio-Labs) confined between them.
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20 Results & Discussion

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22 The crystal structure of the as-synthesized KNNWs was determined using
23 characterization techniques including: SAED, XRD, Raman spectroscopy, and
24 scanning transmission x-ray microscopy. The hydrothermal method used has
25 been characterized extensively [27] and the current results support a monoclinic
26 phase. SEM images clearly show the orthogonal cross sections of KNNWs signi-
27 fying highly crystalline growth (Fig. 1a) with an average edge length measuring
28 152 ± 49 nm, which lies below the single-mode waveguide cutoff for 975 nm in
29 KNbO_3 : 229 nm. However, the inhomogeneous contrast found in the bright field
30 TEM image of an individual KNNW (Fig. 1b) indicates a significant amount of
31 extended crystallographic defects (Fig. 1c) including stacking faults and twin-
32 ning planes. The corresponding SAED pattern (Fig. 1d) confirms a monoclinic
33 phase with a [100] growth direction. Faint lines can also be seen in the SAED
34 pattern which agrees with stacking faults observed in brightfield micrographs.
35 X-ray diffraction (Fig. 1e) and Raman spectra (Fig. 1f) also support a mono-
36 clinic phase. Weak signals can be seen in the XRD plot at 38° and 70° which
37 are not attributable to KNbO_3 and are likely from residual Nb metal precursor.
38 However, analysis of these peaks using the Scherrer equation [28] gives a parti-
39 cle size > 15 nm which are not observed in TEM brightfield images or SAED
40 patterns from individual KNNWs, meaning there is no Nb metal within the
41 KNNWs themselves. Since 1-dimensional KNbO_3 structures are easily identi-
42 fied optically during laser trapping experiments, Nb precursor material can be
43 excluded as a contributing factor for heating of trapped KNNWs.
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The chemical bonding environment surrounding the niobate ion can be probed with scanning transmission x-ray microscopy (STXM). A suspended KNNW was imaged using scanning transmission x-ray microscopy (Fig. 2a) and a linescan of the nanowire was used to extract x-ray absorption in the energy range of 520 - 580 eV. Observation of the O K-edge at 530 eV shows a slight deviation from the simple O 1s $\rightarrow$ O np transition. The XAS absorption profile of KNbO₃ has been explained previously [29] through the hybridization of O 2p and with several different Nb orbitals including 4d (t_{2g}), 4d (e_g), 5s, and 5p. The spectrum measured from our material (Fig. 2b) matches well with the previous report well.

The electric fields generated within an optically-trapped KNNW is of sufficient intensity that the material will respond nonlinearly, described by the second-order polarization:

$$\mathbf{P}(t) = \epsilon_0 \chi^{(2)} \mathbf{E}^2(t). \quad (1)$$

Here ϵ_0 is the permittivity of free space, $\chi^{(2)}$ is the second-order nonlinear susceptibility, and $\mathbf{E}(t)$ is the electric field. Gases, liquids, amorphous solids, and many crystal structures display inversion symmetry and, therefore, have a vanishing $\chi^{(2)}$. KNbO₃, however, is a non-centrosymmetric crystal which will demonstrate second-order nonlinear effects. If a field consisting of two frequency components, expressed as $\mathbf{E}(t) = \mathbf{E}_1 \cos(\omega_1 t - kx) + \mathbf{E}_2 \cos(\omega_2 t - kx)$, is incident on a nonlinear material, it can be seen that, following Eq. 1, the resultant fields will include second harmonic frequencies ($2\omega_1$, $2\omega_2$), the sum frequency ($\omega_1 + \omega_2$), and the difference frequency ($\omega_1 - \omega_2$). In the current experiment, co-aligned lasers of different frequencies are used to demonstrate simultaneous SHG and SFG in trapped KNNWs. In one experiment the 975 and 1064 nm lasers were used to trap the same NW producing their respective second harmonic signals at 487.5 and 532 nm in addition to the sum frequency signal at 509 nm (Fig. 4a). Figure 4b shows the potential of tunable SFG from an optically trapped KNNW. Eleven spectra are overlaid with each spectrum showing SHG from the 1064 nm laser, SHG from the NIR tunable laser set to

a particular wavelength, and the SFG signal from the tuned and 1064 lasers. It can be inferred from these observations that there is also radiation generated at wavelengths corresponding to the difference frequencies: 11.7 μm (106 meV), the difference between 1064 nm + 975 nm and 24.7 - 46.1 μm (27 - 50 meV), the difference between the tunable NIR laser + 1064 nm. However, the estimated power for SHG and SFG signals, accounting for grating and detector efficiencies, is 10^{-14} W and, assuming a similar efficiency for DFG, the mid-infrared powers would be over an order of magnitude less than visible powers. Even with water's high absorption in the mid-infrared, solvent heating due to DFG is unlikely due to negligible powers generated. Figure 4c shows the relative intensities of SHG polarized parallel and perpendicular to the 1064 nm fundamental beam. The ratio of polarization for SHG (~ 10) indicates that the visible luminescence from a trapped KNNW is able to maintain a significant amount of coherence which could be beneficial for applications where lasing is required on a micro- and nano-scale.

Optical trapping of a single nanostructure with parallel end facets also permits the observation of Fabry-Pérot resonances, depending on the particle geometry and wavelength of light. In this case, the second harmonic of the tunable laser lies in the range 510 - 520 nm while the cavity length is approximately 4 micrometers. The mode spacing is expressed [30]:

$$\Delta\lambda = \frac{\lambda^2}{4L[\lambda \frac{\partial n}{\partial \lambda} - n]} \quad (2)$$

where λ is the wavelength, n is the refractive index of the material, $\partial n / \partial \lambda$ is the dispersion of the refractive index, and L is the length of the NW. Using reported [31] values for the optical properties of KNbO_3 , the predicted mode spacing is 6.5 nm which matches well with the experimental value of 5.8 nm. The width of the SHG signal can also be used to comment on the quality factor of the KNNW based on the formula $Q = \omega_0 / \delta\omega$, giving a value of ~ 80 .

Temperatures of particles within an optical trap are often ignored based on assumptions of negligible absorption. But the significant temperature dependence of phase-matching for nonlinear materials requires a better understanding of the

heat generated in these materials under intense illumination. It has been demonstrated that back focal plane interferometry of forward-scattered laser light can be used to monitor the Brownian motion of a trapped NW. [32] In these experiments the forward-scattered laser light is collected and focused onto a quadrant photodiode where the voltage-to-displacement calibration factor is found using a piezo-oscillation method [33]. Once the calibration factor is determined the experimental diffusion coefficient can be found by fitting the calibrated QPD power spectrum [34]. The temperature of the trapped NW can then be determined by equating the experimental diffusion coefficient to the hot Brownian motion diffusion coefficient of a heated particle in a locally non-isothermal environment [35, 36] and solving for the particle's temperature. Temperatures of trapped KNNWs were found using this method and are compared to temperatures of SiO₂ beads at identical trapping powers in Fig. 6. The bandgap of KNbO₃ lies in the ultraviolet region of the spectrum [37] so one would expect little one- or two-photon absorption from the NIR wavelengths used to trap the NW. However, crystal defects can enhance optical absorption within the lattice resulting in heat generation. [38] The inhomogeneous contrast seen in the KNNW bright-field TEM micrograph (Fig. 1b and c) indicates lattice distortion which is further supported by the SAED pattern where the faint linear streaks between spots characteristic of large numbers of extended crystallographic defects. Experimental temperatures can be used in conjunction with recent theory [32] for heating of finite cylinders in order to estimate the imaginary refractive, k of a trapped KNNW. By assuming a circular cylinder with a length of 4.12 μm and diameter equal to the edge length of the KNNW square cross section (150 nm), it is found that $k \approx 0.0005$, which corresponds to an equivalent absorption coefficient of $\alpha \approx 60\text{cm}^{-1}$.

Conclusion

We have demonstrated that the use of a tunable, 1020-1040 nm, continuous-wave NIR trapping source with hydrothermally synthesized potassium niobate

nanowires provides tunable second harmonic generation which can then be used to extract an effective refractive index through Fabry-Pérot mode spacings. Additionally, the range of tunability of the nonlinear emission in the visible region can be extended by introducing a second, co-aligned NIR laser source resulting in sum frequency generation. Given the potential for application of these nonlinear materials in theranostic nanomedicine, the heat generated by nanoscale particles in the intense fields necessary for nonlinear effects could have a significant impact. Temperature measurement through analysis of particle Brownian motion shows an increase from room temperature to $\sim 60^\circ\text{C}$ at an irradiance of approximately 10 MW/cm^2 which we attribute to crystallographic defects evidenced in the contrast from bright field TEM and SAED patterns. Future efforts could exploit the narrow linewidth and tunability of the visible SHG from individual KNNWs, for example, to selectively pump narrowband absorbers like rare-earths or photosensitizers for photodynamic therapy.

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Figure 1: Characterization of hydrothermally grown nanowires. a) Scanning electron micrograph of KNNWs demonstrating square cross-sections. Scalebar = 500 nm. b) Transmission electron micrograph of a single KNNW. Scalebar = 300 nm. c) Higher magnification of KNNW in b to show extended planar defects in a KNNW. Scalebar = 30 nm. d) Select area electron diffraction pattern of the KNNW in b. Scalebar = 5 nm^{-1} e) X-ray diffraction of a KNbO_3 powder sample with crystal planes indicated. Asterisk denotes peaks not associated with KNbO_3 and are likely from Nb metal precursor. f) Raman scattering from a KNbO_3 powder sample.

Figure 2: (a) Scanning transmission x-ray micrograph of KNNWs suspended on a lacey carbon TEM grid. The arrow indicates the line drawn with the linescan used to determine the spectrum in panel (b). X-ray energy for the micrograph is 540 eV. Scalebar = 1 μm . (b) Near edge X-ray absorption fine structure (NEXAFS) of the O K-edge from the monoclinic KNNW linescan in (a) demonstrating the effect of hybridization of the O 2p orbitals with the Nb orbitals.

Figure 3: Schematic of experimental optical trapping setup.

Figure 4: Sum frequency generation. a) Sum frequency generation from a KNNW using co-aligned 975 and 1064 nm lasers. b) Tunable sum frequency generation from a KNNW using a co-aligned 1064 nm DPSS laser and a tunable 1020-1040 nm DPSS laser. c) SHG of 1064 nm fundamental laser with polarizer parallel (black) and perpendicular (red) to the fundamental polarization.

Figure 5: (a) Bright field image of a KNNW in Brownian motion. Scale bar = $2\ \mu\text{m}$. (b) Long-exposure, dark image demonstrating SHG from the KNNW while trapped with a 1030 nm source. Scale bar = $2\ \mu\text{m}$. (c) A NIR tunable laser was tuned from 1020 to 1040 nm while maintaining a constant trapping power (lower panel). The second harmonic generation from a KNNW was detected at each discrete pump wavelength (upper panel). The oscillations with the SHG are due to a Fabry-Pérot resonance within the NW.

Figure 6: Temperatures of trapped KNNWs (squares) and SiO₂ beads (circles) using a 975 nm laser diode (open) or 1064 nm DPSS laser (closed) measured using Brownian analysis of forward-scattered laser light.