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Measurement of the thermal conductivity of a water-based single-wall carbon nanotube colloidal suspension with a modified 3-ω method

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Abstract

A modified 3-ω method applied to a suspended platinum microwire was employed to measure the thermal conductivity and convective heat transfer coefficient of a water-based single-walled carbon nanotube (CNT) solution (metallic single-wall nanotubes with 1.33 nm diameter and 1.14 wt% concentration), and an expression for calculating the convective heat transfer coefficient in such a free convective fluid was introduced. The measurement technique was validated for three model systems including vacuum, air and deionized water. It is found that there is excellent agreement between these three model systems with theoretical predictions. In addition, the frequency dependence on the third harmonic response measured in deionized water reveals the existence of a very low working frequency below 60 mHz. The thermal conductivity and convective heat transfer coefficient of the nanofluid (water-based single-wall CNT solution) were determined to be 0.73 ± 0.013 W m^{-1} K^{-1} and $14\,900 \pm 260$ W m^{-2} K^{-1}, respectively, which correspond to an enhancement of 19.4% in thermal conductivity and 18.9% in convective heat transfer as compared to water.

(Some figures in this article are in colour only in the electronic version)

Nomenclature

c_p	specific heat, J kg^{-1} K^{-1}
D	diameter, m
h	convective heat transfer coefficient, W m^{-2} K^{-1}
I_0	peak current amplitude, A
k	thermal conductivity, W m^{-1} K^{-1}
L	length, m
n	index
R	resistance, Ω
R'	temperature coefficient, Ω K^{-1}
S	cross-sectional area, m^2
t	time variable, s
T	temperature, K
V	voltage, V
x	space variable, m
α	heat diffusivity, m^2 s^{-1}

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θ	differential temperature, K
ρ	density, kg m^{-3}
ω	angular frequency, rad s^{-1}
Subscripts	
0	reference point
3-ω	third harmonic
vac	vacuum
cont	contact

1. Introduction

Determination of the thermal properties of one-dimensional materials such as carbon nanotubes [1, 2], nanowires [3, 4] and their different applications, for example, CNT nanofluids (colloidal suspensions of CNTs), CNT nanoheaters or CNT ultrathin films, has attracted serious research attention in recent years [5–8]. To obtain heat transfer performance data for a system using CNT nanofluids, the knowledge or the determination of the thermal conductivity of this nanofluid is necessary. However, due to the fact that heat flow and temperature measurements have to be controlled at a very small length scale, there are difficulties in measuring thermal properties of such fluids, making these experiments challenging and not always reliable. The reported measured data on the thermal conductivity of nanofluids are scattered over a wide range [9, 10].

There are several methods for measuring the thermal conductivity of nanowires and nanotubes [11–15], while the 3-ω method has received considerable attention as a novel method from many researchers [16–18]. The 3-ω method employs a four-point probe technique (see figure 2 for more details), which detects the third harmonic response to alternating current (AC) excitation at the fundamental frequency. The measured electrical signal (the 'locked' third harmonic voltage) is correlated to the temperature response of a thermal system, and thus to the thermal transport properties such as thermal conductivity. For example, Choi *et al* [16] have implemented the 3-ω method for measuring the thermal conductivity of individual multi-walled carbon nanotubes at room temperature under vacuum conditions. Lu *et al* [18] obtained the specific heat and thermal conductivity of CNT bundles by using the 3-ω method. While the conventional hot-wire method is a time domain transient technique, the 3-ω method has the advantage of measuring electrical signals (3-ω voltage) in a specific frequency domain, which makes the measurement time-independent. The measured signals for thermal conductivity by the 3-ω method are averaged on a sufficiently long time that is much longer than the characteristic timescale for particle motion in the fluid. Thus, this method eliminates the possibility of measuring spurious signals due to the time-dependent particle motion. Furthermore, as compared to a steady state technique that utilizes the fundamental definition of thermal conductivity, $k = (Q/A)/(\mathrm{d}T/\mathrm{d}L)$, the 3-$\omega$ technique introduced in this paper is essentially not affected by radiation heat transfer because the average temperature rise is maintained below 1 K (the ratio of radiation to convection heat transfer is estimated at 0.1% by using radiation/convection $\approx \sigma T^3/h$, where σ is the Stefan–Boltzmann constant, 5.67×10^{-8} W m^{-2} K^{-4} and h is the convective heat transfer coefficient). On the other hand, the testing conditions for the measurement of the thermal conductivity of nanofluids present different challenges. To exemplify, the sensitivity of the thermal properties of a nanofluid to evaporation during measurements can alter the amount of heat loss from the sample, hence the 3-ω signals. Thus, the entire sample (platinum in this study) must be fully submerged in a pool of fluid that is desired to be measured. Moreover, its exposure to a noisy environment may produce spurious signals, which need to be thoroughly removed with a proper filtering technique. Of particular interest in this paper is the measurement of the thermal conductivity and convective heat transfer coefficient of water-based single-walled carbon nanotube colloids by the modified 3-ω method. A suspended platinum microwire was used to investigate the ability of the 3-ω method to measure the thermal conductivity of this nanofluid (purchased from Topnanosys, Inc.). The concentration of the nanofluid was measured at 1.14 wt%. The type and size of the single-wall nanotube were revealed by using a Raman spectrometer (Thermo Scientific). Figure 1 shows the frequency of the radial breathing mode (RBM) from which the size of the nanotube is estimated. According to RBM peak shape and G/RBM height ratio [19], the CNTs used in this experiment have a dominant metallic behavior. The average diameter was measured at 1.33 nm. It should be mentioned that the surfactants used to prevent the agglomeration of the nanotubes in nanofluids will impede the heat conduction because of their dielectric nature. Furthermore, the validity of the 3-ω method for the CNT nanofluid was tested with a model system of deionized water.

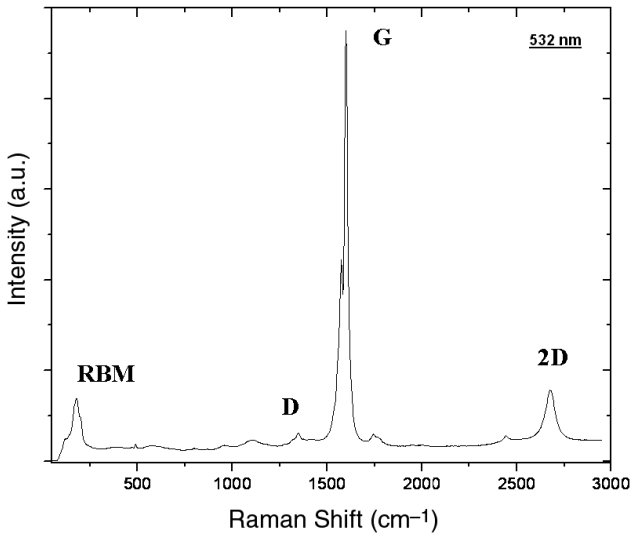

Figure 1. Raman spectrum of the nanotubes used in the nanofluid.

2. Theoretical background

The aforementioned third harmonic response of nanofluids due to fundamental AC current excitation can be correlated to temperature fluctuation along the sensor constructed by a Pt microwire. Therefore, solving the temperature field along the Pt microwire is necessary to obtain thermal conductivity

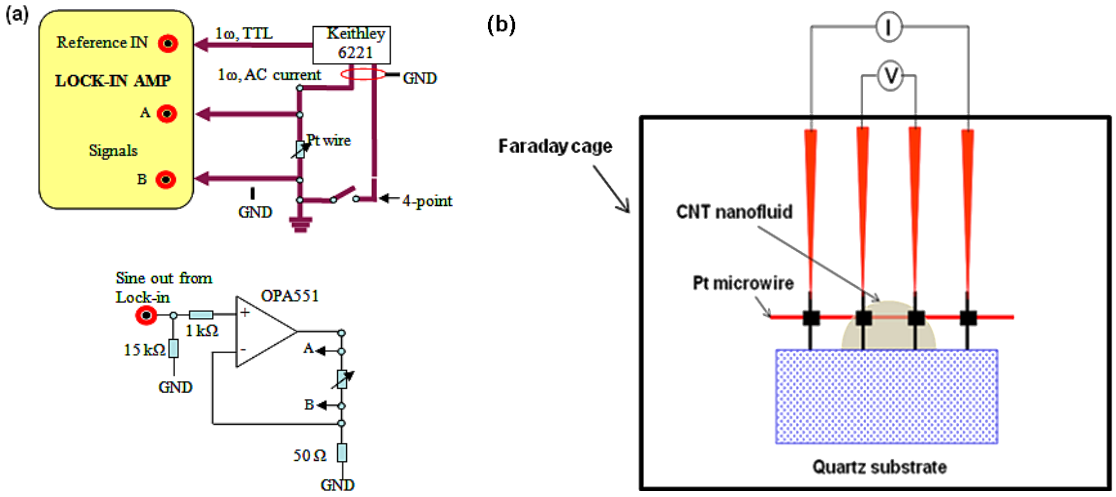

Figure 2. Schematic diagram of measurement set-up; (a) the third harmonic signals generated in the specimen are measured, due to the fundamental AC current excitation; the figure below depicts an in-house circuit for current excitation. (b) Modified 3-ω method set-up coupled with suspended platinum microwire in a Faraday cage. The device consists of four adjacent metal electrodes in which the two inner electrodes are separated by 5.8 mm. All the electrodes are glued to a quartz substrate with highly conductive adhesive.

of nanofluids. The AC current excitation will induce Joule heating along the wire and the wire can be considered as a one-dimensional system because of its microscale dimension. The one-dimensional transient conduction equation along a microwire suspended between two metal electrodes can be utilized to obtain a closed form solution of the third harmonic response of the platinum wire suspended in vacuum [16, 17] (see figure 2(b)) as shown in equation (1):

$$\rho c\frac{\partial T}{\partial t} - k\frac{\partial^2 T}{\partial x^2} = \frac{I_0^2 \sin^2 \omega t}{LS}[R + R'(T - T_0)] \qquad (1)$$

where L, $R[=R_0+R'(T-T_0)]$ and S are the length, electrical resistance and cross-sectional area of the platinum microwire, respectively. R' is the temperature gradient of the resistance at room temperature defined as $(\mathrm{d}R/\mathrm{d}T)_{T_0}$ and k is the thermal conductivity of the platinum microwire. The initial and boundary conditions for the temperature are room temperature (T_0) at time $=$ 0 and at the contacts between the platinum microwire and the metal electrodes, respectively. Lu *et al* [18] modeled the sinusoidal input current represented by the source term in equation (1) as an impulse to the system. In contrast, we employ a Fourier transform technique to derive the same closed form solution for temperature distribution. By defining $\theta = T - T_0$, equation (1) can be rewritten as

$$\frac{\partial \theta}{\partial t} - \alpha\frac{\partial^2 \theta}{\partial x^2} - c_2\theta \sin^2 \omega t = c_1 \sin^2 \omega t \qquad (2)$$

where $c_1 = \frac{I_0^2 R_0}{\rho c_p LS}$ and $c_2 = \frac{I_0^2 R'}{\rho c_p LS}$. Then, the finite Fourier sine transform can be applied to equation (2) to rewrite it as follows:

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t} - \alpha\left(-\frac{n^2\pi^2}{L^2}\Theta\right) - c\Theta \sin^2 \omega t = b \sin^2 \omega t \int_0^L \sin\frac{n\pi x}{L}\,\mathrm{d}x \qquad (3)$$

where $\Theta = \int_0^L \theta \sin\frac{n\pi x}{L}\,\mathrm{d}x$.

Solving equation (3) for Θ and taking the inverse Fourier sine transform, the temperature distribution along the platinum microwire can be obtained:

$$\theta = \sum_{n=1}^{\infty} \sin\left(\frac{n\pi x}{L}\right)\frac{2c_1}{n\pi}[1 - (-1)^n]\xi(t) \qquad (4)$$

$$\xi(t) = \int_{-\infty}^{t} \sin^2 w\tau \cdot \exp\left[\left(\frac{1}{2}c_2 - \frac{n^2\pi^2\alpha}{L^2}\right)(t-\tau) - \frac{c_2}{4\omega}\sin 2\omega(t-\tau)\right]. \qquad (5)$$

In low current limits, the $\sin 2\omega$ term in the exponential term can be neglected. Keeping only the first term in equation (4) (with an error of 1.2%), and obtaining the resistance fluctuation at 2ω expressed by $\delta R = \frac{R'}{L}\int_0^L \theta\,\mathrm{d}x$, the third harmonic component generated in the platinum wire, $V_{3\omega} = IR = I(R_0 + \delta R)$ is expressed as follows:

$$V_{3\omega,\mathrm{RMS}} = \frac{\sqrt{2}I_0^3 RR'}{\rho c_p LS\pi^2}\left(\frac{\pi^2\alpha}{L^2} - \frac{1}{2}c_2\right)^{-1} \times \left(1 + \left[\frac{2\omega}{\frac{\pi^2\alpha}{L^2} - \frac{1}{2}c_2}\right]^2\right)^{-1/2}. \qquad (6)$$

A simpler expression can be obtained when $\frac{\pi^2\alpha}{L^2} \gg \frac{1}{2}c_2, \omega$ or equivalently

$$\frac{I_0^2 R'L}{n^2\pi^2 kS} \ll 1 \qquad (7)$$

$$V_{3\omega,\mathrm{RMS}} \cong \frac{\sqrt{2}I_0^3 RR'L}{\pi^4 kS}. \qquad (8)$$

Equations (7) imply that the measurement should be made with a low current excitation. If measurement is performed in a fluid, a 'free convective' heat loss term must be added to the right-hand side of equation (1), expressed as $4h(T - T_0)/D$, where h and D are the convective heat transfer coefficient and the diameter of the platinum microwire, respectively. Then,

equation (8) can be rewritten for the third harmonic signal in fluids:

$$V_{3\omega,\mathrm{RMS,fluid}} \cong \frac{\sqrt{2}I_0^3 RR'L}{\pi^4 k\left(1+\frac{4hL^2}{\pi^2 Dk}\right)S} \tag{9}$$

Finally, the convective heat transfer coefficient, h, can be obtained from equations (8) and (9):

$$h = \left(\frac{V_{3\omega,\mathrm{vac}}}{V_{3\omega,\mathrm{fluid}}} - 1\right)\frac{\pi^2 Dk}{4L^2}. \tag{10}$$

The relation between the convective heat transfer coefficient and the thermal conductivity of a free convective fluid can be expressed by considering random diffusion of mass and the natural convective motion of the fluid particles. The Nusselt number represents the ratio of convective to conductive heat transfer and is essentially a dimensionless heat transfer coefficient. It was theoretically calculated from the natural convection correlation. The calculated values are 0.36 and 0.41 for air and water, respectively [20]. The value, 0.36, which was calculated for air corresponds to random mass diffusion only in which case the Rayleigh number is around 10^{-7}. This excludes the presence of non-negligible free convective motion. The Nu_D for the nanofluid is equal to that of water because the solution is mainly composed of water. Furthermore, the thermophysical properties of nanofluids that are dominant factors in the free convective heat transfer (such as viscosity and heat diffusivity) are nearly the same as those of water, which was revealed in this study (i.e. thermal conductivity of nanofluids is close to that of water). To prove this, the viscosity and heat capacity (heat capacity, ρC_p = thermalconductivity/heat diffusivity) of the nanofluid were measured. The viscosity was measured at 1.1 cP (at 21.2 °C) by using an Ubbelohde viscometer with 0.2% uncertainty. The value is 10% higher than that of water. The heat capacity was measured at 4.86 J cm^{-3} K^{-1} by using a differential calorimeter (Perkin Elmer DSC 6). Using these data, one can show that the actual Nu_D for the nanofluid varies only within 0.5% as compared to that for water. Therefore, the thermal conductivity of the nanofluid can be written as

$$k_\mathrm{fluid} = \left(\frac{hD}{Nu_\mathrm{D}}\right). \tag{11}$$

Substituting equation (10) into (11) gives

$$k_\mathrm{fluid} = \left(\frac{V_{3\omega,\mathrm{vac}}}{V_{3\omega,\mathrm{fluid}}} - 1\right)\frac{\pi^2 D^2}{4L^2}\frac{k}{Nu_\mathrm{D}}. \tag{12}$$

3. Experimental set-up and procedure

This section describes an experimental set-up for measuring the thermal conductivity of single-walled CNT nanofluids. The experimental method is similar to the 3-ω method employed for measuring thermal conductivity of thin films. The three major components of the experiment are a lock-in amplifier (Stanford Research System, SR850), a precise current source (Keithley 6221) and a modified sample holder encapsulated by a Faraday cage, which are depicted in figure 2. Detailed descriptions about the lock-in amplifier and the current source used herein are published elsewhere [16, 17]. The two important lock-in parameters utilized in the current study were set at 5 mV full scale and maximum dynamic reserve. For the third harmonic signal, the maximum current was limited at 20 mA to minimize the effect of radiation heat transfer and to meet the requirement of low current limits. To block out and remove external static electrical charges a Faraday cage was used and connected to an earth ground.

To check the validity of the proposed method, the thermal conductivity of a platinum microwire (Goodfellow, 20 μm in diameter and 5.8 mm in length) has been measured in vacuum to be within 5% of the literature value [16–18]. To prevent the air convection influence on the thermal conductivity measurement the platinum microwire with four contacts was suspended in vacuum (6×10^{-3} mbar) without touching the substrate, as shown in figure 2(b). In order to have an ideal heat sink at the contacts, a quartz substrate was used and the boundary conditions of the contacts were kept at the substrate temperature. Moreover, the third harmonic response was measured in air and water to check the validity of the proposed theory. Both the in-house (lower figure) in figure 2(a) and a commercial current source (Keithley 6221) have been utilized and the measurement results turned out to be identical within the measurement error margin of the current study. For water and the water-based carbon nanotube solution, we implemented the experimental configuration depicted in figure 2(b). The platinum wire is fully submerged in the nanofluid during the entire experiment. It should be mentioned that all the measurements were made at room temperature and the temperature inside the Faraday cage was kept constant.

4. Results and discussion

It is interesting to note that there exists a range of very low working frequencies for the measurement of water and nanofluids. Repeating the experiments confirmed the existence of these low working frequencies for water and nanofluids. Near-direct-current-like excitation was applied to the Pt wire to negate the artifact caused by the spurious AC response of the nanofluid.

Figure 3 shows measured 3-ω signals at different frequencies for the Pt wire submerged in deionized water. Two main regions are distinguished: no variation of 3-ω signals was detected at frequencies below 60 mHz while there is a sharp increase above this value. As expected, for the water-based carbon nanotube solution the same frequency range was observed and the third harmonic signals became frequency-independent for frequencies lower than 50 mHz. Accordingly, hereafter, to avoid possible uncertainties, the working frequency is set to 50 mHz for all measurements.

In figure 4 variations of the 3-ω signals versus current are plotted for three model cases (vacuum, air and deionized water) and the water-based carbon nanotube solution at room temperature. The signals measured under vacuum are drastically higher than three other systems because the heat loss due to convection and radiation is essentially neglected. The measured thermal conductivity is the same as reported

Table 1. Comparison between measured thermal conductivity and convective heat transfer values obtained by the modified 3-ω method with reference data.

Fluid	Measured k, (W m^{-1} K^{-1})	Reference k, (W m^{-1} K^{-1})	Measured h, (W m^{-2} K^{-1})	Predicted h, (W m^{-2} K^{-1})
Vacuum[a]	70.5 ± 2	71.6	N/A	N/A
Air	$0.0270 \pm 0.000\,11$	0.0267[b]	470 ± 20	480
Water	0.66 ± 0.027	0.611[b]	$13\,567 \pm 550$	12525
CNT fluid	0.73 ± 0.013	N/A	$14\,900 \pm 260$	N/A

[a] These values correspond to suspended platinum microwire.
[b] The measured values are compared to reported data of [20].

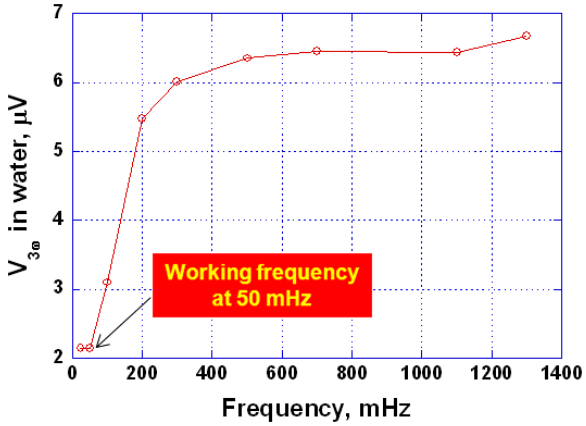

Figure 3. Frequency dependence of $V_{3\omega}$ signals for deionized water at room temperature.

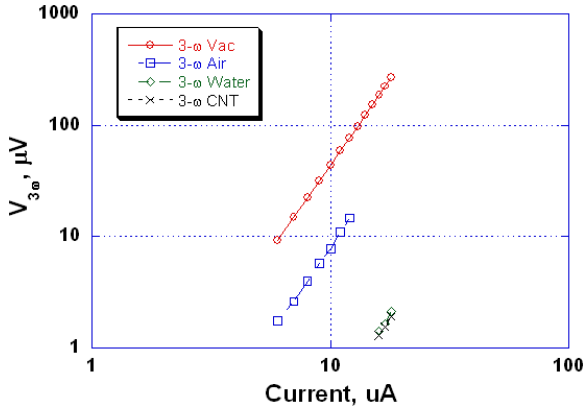

Figure 4. The third harmonic voltage measurements for water-based single-walled carbon nanotube solution at room temperature. The best-fit exponents for all four cases are very close to 3.0, which supports the validity of the modified 3-ω measurement in nanofluids.

elsewhere [20]. The 3-ω signals measured in vacuum and air follow the third power law as shown in equation (8). The exponents were obtained to be 3.0 in vacuum and 2.9 in air. On the other hand, the best-fit exponent obtained for the wire submerged in deionized water and nanofluid turned out to be 2.7, both of which are close to the third power law.

Table 1 shows a comparison between measured values of thermal conductivity and convective heat transfer coefficients and those obtained by natural convection theory. The convective heat transfer coefficients for air and water were obtained to be 470 ± 20 and $13\,567 \pm 550$ W m^{-2} K^{-1}, respectively, by using equation (10).

The thermal conductivity measured in the nanofluid is enhanced by 19.4% while there is a 18.9% enhancement in the convective heat transfer as compared to water, which is attributed to the contribution of suspended single-walled carbon nanotubes. While we measured the thermal conductivity of the nanofluid with reasonable accuracy, the investigation of the convective heat transfer can be challenging due to a lack of knowledge of the thermophysical properties of nanofluids. Moreover, aggregation of nanoparticles can, in general, have an impact on the value of thermal conductivity with time [21]. Such agglomeration was not observed in this study in the nanofluid solution in which there is no visible sediment or separation of the solution. In fact, because there is essentially no temperature rise in the solution, the segregation of nanoparticles is not as conspicuous as in other techniques such as the transient hot-wire utilized by Eastman and Choi [8]. Another advantage of the modified 3-ω method (or 3-ω methods in general) is that it can remove possible uncertainties due to the transient motion of the particles as it employs a time-independent frequency domain technique. Additionally, the range of frequencies that shows the best third power law fit for water and nanofluid is in a much lower regime (<60 mHz) as compared to theoretical predictions [18] while the best-fit exponent for all cases is very close to 3, which proves the accuracy and capability of the modified 3-ω method. Major sources of measurement uncertainty originate from diameter (3%) and length (2%) measurements of the microwire. A series of measurements are best fitted to the third power law to extract the thermal conductivity and heat transfer coefficients within the specified measurement errors (see table 1).

5. Conclusions

In summary, we utilized the modified 3-ω method to measure simultaneously the convective heat transfer coefficients and thermal conductivity of a water-based single-walled carbon nanotube solution. An equation for calculating the convective heat transfer coefficient by measuring 3-ω signals was introduced herein. In addition, calibration and validation of the method was performed for three model systems of vacuum, air and deionized water. The thermal conductivity and the convective heat transfer coefficient measured by this technique were found to be 0.73 ± 0.013 W m^{-1} K^{-1} and

14 900 ± 260 W m^{-2} K^{-1}, respectively, at room temperature. This technique can be extended to the measurement of the thermal conductivity and convective heat transfer coefficient of more complex fluids such as biological fluids and colloids.

Acknowledgment

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References

[1] Prasher R 2007 *Appl. Phys. Lett.* S **90** 143110
[2] Wensel J, Wright B, Thomas D, Douglas W, Mannhalter B, Cross W, Hong H and Kellar J 2008 *Appl. Phys. Lett.* **92** 023110
[3] Moore A L, Saha S K, Prasher R S and Shi L 2008 *Appl. Phys. Lett.* **93** 083112
[4] Lacroix D, Joulain K, Terris D and Lemonnier D 2006 *Appl. Phys. Lett.* **89** 103104
[5] Yoon Y H, Song J W, Kim D, Kim J, Park J K, Oh S K and Han C S 2007 *Adv. Mater.* **19** 4284–7
[6] Jang S P and Choi S U S 2006 *Appl. Therm. Eng.* **26** 2457–63
[7] Roy G, Palm S J and Nguyen C T 2005 *J. Therm. Sci.* **14** 362–7
[8] Eastman J A, Choi S U S, Li S, Yu W and Thompson L J 2001 *Appl. Phys. Lett.* **78** 718–20
[9] Bourgeois O, Fournier T and Chaussy J 2007 *J. Appl. Phys.* **101** 016104
[10] Gupta A and Kumar R 2007 *Appl. Phys. Lett.* **91** 223102
[11] Shi L, Hao Q, Yu C, Mingo N, Kong X and Wang Z L 2004 *Appl. Phys. Lett.* **84** 2636–40
[12] Li D, Wu Y, Kim P, Shi L, Yang P and Majumdar A 2003 *Appl. Phys. Lett.* **83** 2934–6
[13] Wang J and Wang J 2006 *Appl. Phys. Lett.* S **88** 111909
[14] Bryning M B, Milkie D E, Islam M F, Kikkawa J M and Yodh A G 2005 *Appl. Phys. Lett.* **87** 161909
[15] Vavro J, Llaguno M C, Satishkumar B C, Luzzi D E and Fischer J E 2002 *Appl. Phys. Lett.* **80** 1450–2
[16] Choi T Y, Poulikakos D, Tharian J and Sennhauser U 2005 *Appl. Phys. Lett.* **87** 013108
[17] Choi T Y, Poulikakos D, Tharian J and Sennhauser U 2006 *Nano Lett.* **6** 1589–93
[18] Lu L, Yi W and Zhang D L 2001 *Rev. Sci. Instrum.* **72**
[19] Dresselhaus M S, Dresselhaus G, Saito R and Jorio A 2005 *Phys. Rep.* **409** 47–99
[20] Mills A F 1995 *Heat and Mass Transfer* (Boca Raton, FL: CRC Press)
[21] Gharagozloo P E, Eaton J K and Goodson K E 2008 *Appl. Phys. Lett.* **93** 103110