Effect of laser irradiation on thermal conductivity of ZnO nanofluids

Jonggan Hong, Sang Hyun Kim, and Dongsik Kim
Department of mechanical engineering, POSTECH, Pohang 790-783, Korea
E-mail: dskim87@postech.ac.kr

Abstract. This work examines a laser particle fragmentation process to enhance the thermal conductivity of nanofluids. A Q-switched Nd:YAG laser is employed to change the size of the suspended ZnO nanoparticles in water. The influence of laser irradiation on the suspended particles is analyzed by transmission electron microscopy and absorption spectroscopy. The thermal conductivity of the nanofluid is measured by the transient hot-wire method. The results show that laser irradiation leads to partial fragmentation of some particles. However, the partial size reduction results in substantial enhancement of the thermal conductivity.

1. Introduction

Nanoparticles suspended in liquid solutions, so called “nanofluids,” are important in various fields of science and engineering as they exhibit unique physical properties which are significantly different from those of the base liquid or the particles in the bulk state. Particularly, metal or metal-oxide nanofluids have attracted substantial attention because of the enhanced thermal conductivity of the mixture. It has long been recognized since Maxwell first suggested his mixture theory [1] that suspending solid particles in liquids would substantially increase the effective thermal conductivity. Numerous investigations have thus been performed on high thermal conductivity nanofluids [2-5]. In this work, the thermal conductivity variation by high-power laser irradiation onto a ZnO/water nanofluid is experimentally analyzed. Previous studies demonstrated that high-power laser irradiation can result in significant size reduction and shape transformation in the nanoparticles [6-9]. According to those studies, the laser post treatment process is not only a convenient way of changing the particle size but also an effective way to modify the shape and size distribution. In this regard, this work analyzes, for the first time to our knowledge, the behavior of thermal conductivity of nanofluids subjected to UV pulsed laser irradiation. The thermal conductivities of ZnO/water nanofluids are first measured by the transient hot-wire method for three different mean particle sizes, 10, 30, and 60 nm. A Q-switched Nd:YAG laser is then employed to change the size of the 60 nm ZnO nanoparticles in water. The variation of the thermal conductivity of the laser-treated nanofluids is measured at three different laser fluences around the laser ablation threshold. The change in particle size and shape is analyzed by the transmission electron microscopy (TEM) and absorption spectroscopy.
2. Experiment

Figure 1. Transmission electron micrographs ZnO-water nanofluids with the average particle size of (a) 60 nm, (b) 30 nm and (c) 10 nm.

Zinc oxide (ZnO) nanoparticles are mixed with the base fluid water at a volume fraction of 1 % to synthesize nanofluids. The particles are commercial products from Meliorum Technology, Advanced Materials, and Nanophase Technology and have nominal mean diameters of 10, 30, and 60 nm, respectively. Figure 1 displays the typical TEM images of the particles. In the synthesis of the nanofluids, the suspension was sonicated in an ultrasonic bath for an hour and then agitated for 10 hours by a magnetic stirrer to ensure homogeneity and stability of the solution. SDS (sodium dodecyl sulfate) 0.05 M was added as a surfactant in all cases. The surfactant concentration has been chosen to be well above the critical micelle concentration 0.01 M. Addition of the surfactant obviously affects the thermal conductivity of the nanofluid and thus introduces ambiguities in the analysis. Nevertheless, it was unavoidable to prevent particle sedimentation. With the surfactant, no change in the thermal conductivity has been detected at least for the initial 5 hours after synthesis of the nanofluid. The long-term stability of the nanofluid and its effect on thermal conductivity were not analyzed in the present work. To monitor the variation of the particle size in the nanofluid solution, the absorption spectrum has been measured by a UV-visible spectrometer (wavelength $\lambda$=250~800 nm). The absorption spectrum of the original untreated nanofluids was measured as a reference for three different mean diameters 10, 30, 60 nm and the results are displayed in figure 2.

The laser fragmentation process is depicted in figure 3. A Q-switched Nd:YAG laser ($\lambda$=355 nm, full width at half maximum FWHM=6 ns) was employed to ablate particles suspended in the nanofluid. The quartz cuvette in figure 3 initially contains 60 nm ZnO particles at a volume concentration of 1 %. Zinc oxide was selected to analyze the effect of laser irradiation as it strongly absorbs UV light. The laser pulses having a fit-to-Gaussian spatial distribution of intensity and a spot size of 5 mm are incident on the liquid at a frequency of 10 Hz. The nanofluid is irradiated for an hour, i.e., 36000 pulse, at three different laser fluences 310, 460, and 610 mJ/cm². The transient hot-wire method has been employed to measure the thermal conductivity after the laser fragmentation process. Principles and

Figure 2. Absorbance peak wavelengths as a function of particle mean diameter.

Figure 3. Schematic diagram of the laser fragmentation process for nanofluid size reduction.
details of the measurement technique can be found elsewhere [10, 11]. In this work, a tantalum wire of 25 μm in diameter and 54.0 mm in length was anodized for electrical insulation. A bare tantalum wire was electrically heated at an electrical potential of 50 V in a citric acid solution at 0.01 wt % to form the oxide layer for electrical insulation [12]. To confirm the experimental setup, the thermal conductivity of standard liquids was measured. The results show that the measured thermal conductivities are 0.131, 0.607, 0.252 W/m-K for toluene, de-ionized water and ethylene glycol, respectively, with deviations from the literature values [13,14] by 0.3, 0.8, and 0.1 %. Measurements were repeated 10 times for a sample and the averaged value was taken to be the thermal conductivity of the sample. The maximum random error in the measurement was 0.6 %. These results demonstrate that the experimental setup used in the present study can produce a reliable data.

3. Results and Discussion

The measured thermal conductivities of the nanofluids containing 10, 30, and 60 nm-sized ZnO particles are 0.637, 0.627, and 0.618 W/m-K at 20°C, respectively, at a volume fraction of 1 % while that of pure water is 0.607 W/m-K. Note that the thermal conductivity of ZnO is 29 W/m-K at 46°C [14]. The enhancement ratio relative to pure water is therefore 1.8~4.9 %. The enhancement ratio increases with the volume fraction and reaches 7.3~14.2 % at 3 % volume fraction. The measured thermal conductivity of the nanofluid is inversely proportional to the mean size of the suspended particles at a fixed volume fraction, suggesting that the laser fragmentation process can increase the thermal conductivity.

The apparent ablation threshold for ZnO particles in water was measured by monitoring the absorption spectrum and absorbance. If the laser fluence incident on the glass cuvette is less than 300±30 mJ/cm² (58 mJ/pulse), no significant changes were observed in the optical absorption spectrum and absorbance. Therefore, the nanofluid composed of 60 nm sized particles was irradiated by the UV laser pulses at three different laser energies 60, 90, and 120 mJ/pulse. The thermal conductivity of the laser-treated nanofluids was measured after 36000 pulses and the measured values are 0.618, 0.624, and 0.626 W/m-K for laser fluences 310, 460, and 610 mJ/cm², respectively. Compared to the thermal conductivity of the untreated nanofluid, it is evident that the laser fragmentation process increases the thermal conductivity by decreasing the size of the suspended particles. The thermal conductivity of the 60 nm nanofluid processed at 610 mJ/cm² is close to that of the 30 nm unprocessed nanofluid as depicted in figure 4. Notable is that the incident laser fluence is

![Figure 4](image-url)  
**Figure 4.** Effective thermal conductivity of nanofluids after laser irradiation at different fluences (36000 pulses).

![Figure 5](image-url)  
**Figure 5.** TEM images of ZnO nanoparticles after laser irradiation below and above the threshold laser fluence (left: 310 mJ/cm², right: 610 mJ/cm²).
above the ablation threshold but not high enough to cause complete fragmentation of the suspended particles. At the present fluence level, most of the particles are only partially ablated with a relatively low fragmentation efficiency. Our previous investigation on laser fragmentation of small particles indicated that the ablation threshold is substantially lower than that required for the same material in the bulk form but the particles are only partially fragmented unless the laser fluence is substantially above the threshold value [15]. The TEM analysis clearly shows the changes in the nanoparticles by laser irradiation. Figure 5 exhibits typical TEM images of the ZnO particles after the laser fragmentation process. Compared to the image in figure 1(a), figure 5(a) does not show significant changes in the particle shape and size. On the other hand, figure 5(b) shows several small particles generated by the fragmentation process. If a majority of the particles went through the fragmentation process, there would be a frequency shift in the absorption peak as indicated in figure 2. However, the absorption spectrum analysis shows no changes in the absorbance peak at all laser fluences, with the peak being always around 375 nm. Consequently, the enhancement of thermal transport is believed to be due to partial fragmentation of the particles. It is thus evident that size reduction, even though partial, increases the nanoscale mixing effects, such as Brownian motion and liquid clustering [5].

4. Conclusion
In this work, the effect of the laser fragmentation process on the effective thermal conductivity of a nanofluid has been experimentally analyzed. The analysis of TEM, absorption spectrum, and thermal-conductivity reveals that high-power laser irradiation leads to fragmentation of a small fraction of the suspended particles with a significant increase in the effective thermal conductivity. Consequently, this work demonstrates the feasibility of using the laser fragmentation processes as an effective method for thermal-conductivity enhancement.

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