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# Photothermal properties of graphene nanoplatelets nanofluid for low-temperature direct absorption solar collectors

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ABSTRACT

Today's population growth and increasing dependency of industry and technology on fossil energy encounters all countries and communities with challenge of energy for future. Hence researches about renewable energies, especially solar energy are considered. Among all types of solar systems, the optimization of direct absorption solar collector performance which the solar radiation received by the fluid medium, have been investigated. Since nanofluids are considered as an appropriate environment to absorb solar energy as well as increase in heat transfer coefficient, in present work, the morphological structure, the stability, the optical properties and thermal conductivity of nanofluid have been investigated by preparing nanofluid containing graphene nanoplatelets on the bases of deionized water by 0.00025, 0.0005, 0.001 and 0.005 wt%. Finally, by investigating the effect of weight percent and temperature of nanofluids on optical properties and thermal conductivity, this nanofluid with strong absorption band in the range of 250–300 nm as a suitable environment is offered to be used in direct absorption collectors.



## 1. Introduction

Since sun is available in most parts of the world it is considered as a source of renewable energy. The amount of solar energy absorbed by Earth's atmosphere, land surface and the ocean is about $4 \times 10^{24}$ J per year, due to the amount of energy absorbed by the Earth during one hour it can provide energy consumption more than a year of a world [1]. In 1970s, there was an oil crisis and considerable researches have been done in relation to solar energy by various researchers [2]. In 1980s and 1990s, by reducing the oil crisis, the investigation slope went slower than the past, so that in recent years, according to the crisis of energy supply, again using solar energy as an attractive area is taken into attention of researchers. According to the investigation of the types of technologies of solar energy, it is clear that the conversion and use of photo-thermal are important because apart from using in heating systems [3], it is used in electricity generation [4] and chemical technologies [5]. In solar heating systems, collectors are the most important part in conversion of photo-thermal. Among all types of solar collectors, volumetric absorption or direct absorption collector have high efficiency due to the light from volume of fluid instead of limiting it to the surface and also receiving the heat emitted by the heated surfaces [6]. Among the benefits of volumetric absorptions in comparison with surface absorber, it can be noted that the solid particles suspended in suspension used in volumetric collectors are able to absorb the solar energy and since these particles are in contact with fluid, they transfer their receiving energy to the surrounding fluid. Existing particles in fluids cause increased levels that can absorb more energy and transfer convection heat [7]. A century ago, in order to increase heat transfer and thermo-physical properties of fluid, the idea of dispersing solid particles in fluid was discussed [8]. Nanofluid is the fluid containing metallic or non-metallic solid particles with an average diameter less than 100 nm. It should be noted that the term “nanofluids” was first used by Choi for a new group of fluids containing solid particles [9]. Studies show that nanofluids have better thermo-physical properties than basic fluids such as water or ethylene glycol and oil [10–12]. Another advantage of the nanoparticles is radiative properties of basic fluid and improving their ability to absorb radiant energy [13]. This advantage beside thermal properties causes that using nanofluids in direct solar absorption collectors is taken into attention [14–17]. Otanicar et al. [18] have done the first experimental study on direct absorption collectors by using nanofluids of graphite, carbon nanotubes and silver on the bases of water and the results showed that using nanofluids increase optical properties of fluid and it can also increase the efficiency of the solar collector to be about 5%. Taylor et al. [19] showed that in different situations nanofluids are able to absorb 95% of radiant energy by investigating the optical properties

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of nanofluids containing particles of graphite, gold, copper, aluminum and silver. Mu et al. [20] considered the importance of using nanofluid in volumetric collectors by using nanofluids of Titanium Oxide, Silicon Oxide, Zirconium Carbide on the bases of water. The results showed that using Zirconium Carbide nanoparticles in water has a significant impact in increasing the amount of solar energy compared with other nanofluids. In experimental study which Bandera et al. [21] have done by using silver nanoparticles in a direct absorption of solar, they concluded that nanofluids with the volume fraction of 6.5 ppm can increase system performance up to 144%. Liu et al. [22] with numerical and experimental study investigated the use of graphene in ionic fluid in direct absorption collector at high temperature. Their research results showed that receiver with weight percent of 0.0005 at a height of 5 cm of nanofluids and under radiation of $20 \times 1000\ \mathrm{W\,m^{-2}}$ at a temperature of 600 K has a performance of 0.7. Said et al. [23] showed that Titanium Oxide compared to Aluminum Oxide has a better optical properties by experimental measurements and investigating optical properties of nanofluids with metal oxide particles. Karami et al. [24] by introducing new applications of nanofluids containing Carbon Nanotubes in direct solar absorption collectors at low temperature investigate an optical properties of nanofluids and the results of their research showed that using these nanoparticles in volume fraction of 150 ppm will increase thermal conductivity up to 32%. Zhang et al. [25] introduced suitable nanofluid for using direct absorption collectors at medium to high temperature by investigating the optical properties of nanofluids on the bases of ionic fluid. Their research results show that nanofluids with the volume fraction of 10 ppm containing Nickel nanoparticles has better performance than nanofluids containing Copper with the same volume fraction. They also investigated nanofluid properties containing Carbon particles coated with Nickel compared to nanofluid containing pure Nickel concluded that nanofluids containing Carbon coated with Nickel in volume fraction of 40 ppm can absorb nearly 100% energy and has better performance than pure Nickel. Shende et al. [26] used nanofluids particles containing Multi-Walled Carbon Nanotubes and Graphene Oxide which is strengthened by nitrogen in order to use direct absorption collectors in low-temperature. Their research results show that using this type of particle in water with volume fraction of 0.02 percent increase 17.7 percent thermal conductivity and also using these particles in Ethylene Glycol with volume fraction of 0.03 percent increase up to 15.1 percent. Due to the importance of base fluid and suspended particles in a volumetric collectors or direct absorption, the optimization of solar collectors will happen by directly absorbed mechanism when suitable base fluid is used. Thus, the importance of using graphene nanoplatelets as an agent particle in water has been investigated.

## 2. Experimental method

### 2.1. Material and method of preparing nanofluids

Deionized water and graphene nanoplatelets with diameter less than 2 μm and the thickness of graphene nanoplatelets is 2 nm with the surface area of $750\mathrm{m^2\ gr^{-1}}$ were used to produce nanofluids and provided by Grade C, XG Sciences, Inc., Lansing, MI, USA. Preparing stable nanofluids with uniform distribution is essential for measuring thermo-physical and radiative properties. Among the existing methods for preparing nanofluids, the two-step method is used. In this method, a certain amount of nanoparticles with 0.00025, 0.0005, 0.001 and 0.005 wt%. is dispersed by using ultrasonication probe (Q700 Sonicator, Qsonica, LLC.,USA) which has a power of 700 W and a frequency of 20 kHz in deionized water. Ultrasonic time length for making samples is an hour with power of 95% and for preventing extra heat of fluid, the mixture is alternately ultrasonic probe. In Fig. 1 the prepared samples are shown.

### 2.2. Method of investigating the properties

Two methods are used for analyzing materials and investigating the structure of prepared ones. One of the methods which was chosen to investigate the morphology of graphene nanoplatelets structure is the method of transmission electrons microscopes. This method used the transmission electrons microscopes (TEM,EM900, Zeiss,Germany), with an acceleration voltages of 80 kW. Fig. 2 shows the image of graphene nanoplatelets layer in specific surface area 750 $\mathrm{m^2\ gr^{-1}}$. The graphene nanoplatelets include sheet-like structure with a lateral size at the micrometer length scale that is shown in Fig. 2 as well. The graphene nanoplatelets sheets only contain a few number of Graphene layers, which are compatible with the manufacturer parameters. When graphene nanoplatelets were dispersed by ultrasonic probe, the lateral size of graphene nanoplatelets was decreased. With nanofluids defined preparation method, the edges of GNP layers are clearly seen. The ultrasonic process tends to break the flake, therefore; the longer process time improves dispersion of nanoparticle in base fluid.

Another way which is used to evaluate chemical composition and crystalline structure of material is X-Ray Diffraction. In this way, X-Ray Diffraction (PANalytical, XPert Pro MPD,Netherlands) with an angle range of measure 0.6–157° is used. Fig. 3 shows the XRD pattern of Garphene Nanoplatelets. The maximum value of the peak in diagram is related to sample preparation and measurement equipment. The peak position appears at $2\theta = 26.31$, which is close to that of single crystalline graphite ($2\theta = 26.5$). This peak is different from turbostratic graphite ($2\theta = 25.8$). These results clearly demonstrate that this material possesses a crystalline structure.

There are several ways to assess the stability of prepared nanofluids: deposition methods, zeta potential and absorption spectrum method. Here zeta potential is used to seek stability of nanofluids. Zeta potential of nanofluid is measured, by using Zetasizer Nano devices (ZEN 3600, Malvern Instruments Ltd, UK). Optical properties and the

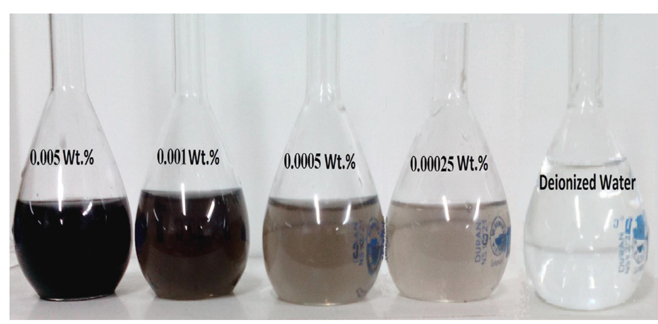


**Fig. 1.** Samples of the nanofluids by different weight percent.

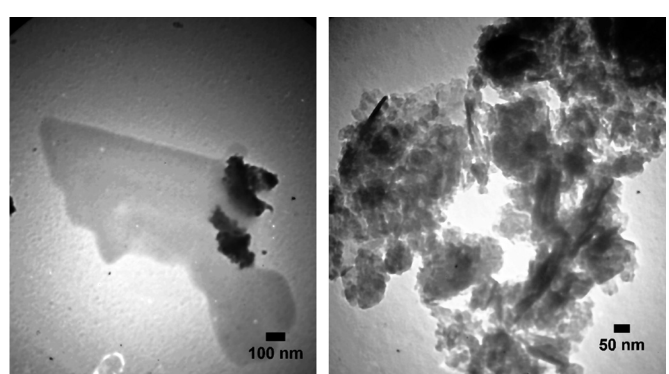


**Fig. 2.** TEM images of graphene nanoplatelets.

amount of Transmittance spectra are measured by using UV–vis–NIR spectrophotometer (Cary 5, Varian Inc., USA). Quoet is made from quartz with a length of 10 mm in this experiment. To ensure the performance and calibration as well as minimizing measurement error, first deionized water sample is compared with itself then with nanofluids.For measuring nanofluids thermal conductivity, the transient hot wire method was used by the device (KD2 Pro, Decagon devices Inc., USA) in a temperature range of 25–50 °C.

## 3. Results and discussion

### 3.1. The stability of nanofluids

Deposition of nanoparticles in the base fluid, not only contributes to clogging of the channels, but also reduces thermal conductivity. Hence stability is a key issue that has an impact on nanofluids properties and it is essential to study the characteristics affecting it. Most of the liquids contain cation and anion that is ions or atoms with positive and negative charges. When charged particles suspend in liquid, the ions of opposite charge attract to the suspended particles. The stability of colloidal system is determined from total absorbed forces of van der Waals and disposed electrical double layer between particles which occurs due to Brownian motion. Generally, the zeta potential of 25 mV (positive or negative) is introduced as the border amount in nanofluids stability [27], that the zeta potential of nanofluids with more than +30 and less than −30 have good stability [12]. According to the measurements, prepared nanofluids from graphene nanoplatelets having zeta potential is −31.2±0.5 which shows the stability of nanofluids. Fig. 4 shows the measurement results. Considering that all nanofluid samples were prepared in the same method, by measuring the zeta potential which has the highest weight percent, we can determine and investigate the samples stability. In addition, by the investigations that have been done visually, the dispersed nanoparticles in samples have a tendency to sedimentation after 45 days.

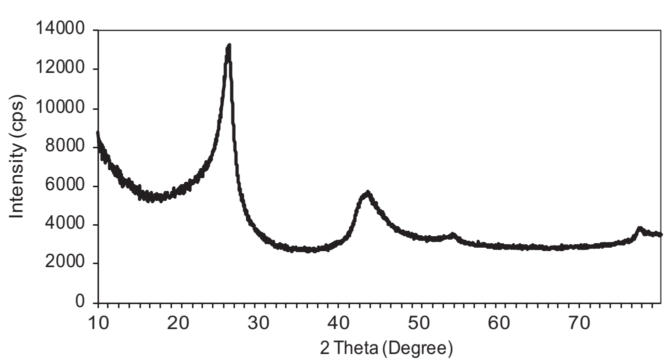


**Fig. 3.** The results of X-ray diffraction graphene nanoplatelets.

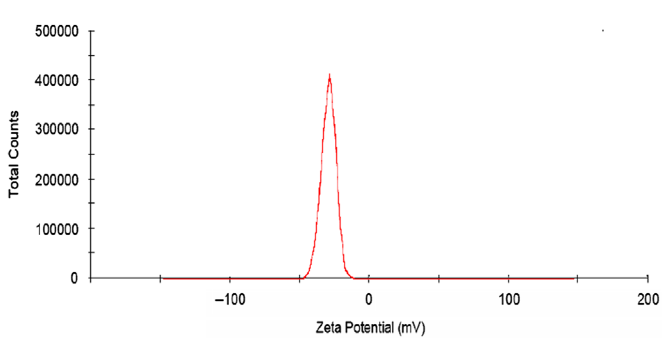


**Fig. 4.** Zeta potential value of nanofluid with weight percent of 0.005.

### 3.2. Optical properties of nanofluid

The ability to sync with the spectrum of solar radiation is the characteristic which distinguishes direct absorption and volumetric absorbers from surface absorbers. In this section, how the particles dispersed in the fluid on radiative properties has been studied, because the weight percent of particles can be adjusted in a way that nanofluids can absorb the total solar energy. Therefore, the results of the transmittance coefficient from nanofluids compared to the amount of solar energy per wavelength is shown in Fig. 5.

According to the results shown in Fig. 5, nanomaterials reduce the transmittance coefficient significantly through the base fluid, thus the amount of absorbed light will increase. Due to investigating the importance of nanofluids concentration in the amount of absorption, the samples are made and investigated at different weight percent. Hence, the sample of nanofluid in 0.005 wt% absorbed almost all of the light emitted, there is no need to prepare a higher weight percentage, because the results of the higher weight percentage is the same as the result of 0.005 wt%, therefore, samples with less weight percentage and with a specified ratio are prepared and tested. The intermediate portion of the spectrum of sun includes a portion of the visible and infrared (IR) that is termed thermal radiation because it is both caused by and affects the thermal state or temperature of matter. Strong absorption band in nanofuids is in the range of 250–300 nm (this range of wavelengths is in the visible region of the sun). This means at higher graphene nanoplatelets concentrations, about 100% sunlight absorption is obtained within the thin layer of the liquid flowing in the typical solar thermal receiver. Absorption is completely done also between 1400 and 1550 and more than 1850 nm, due to the opaque nature of nanofluids. As a result, it is important to select a suitable material of nanoparticles for the nanofluid to be used as the absorbers in DASCs. Hence, graphene nanoplatelets/deionized water nanofluid can be used in solar thermal systems as well as direct absorption or volumetric solar collectors. Light absorbency ratio index can be calculated by using Bear–Lambert law with Eq. (1) and the results are shown in Fig. 6:

$$A = -\log\left(\frac{I}{I_o}\right) \quad (1)$$

where $I$ is transmitted light intensity and $I_o$ is incident light intensity.

Since solar wavelength in visible area has the most amount of radiation and thermal properties and this wavelength is important in direct absorption collectors, it can be useful in direct absorption collectors due to the Graphene absorption band. To better study the radiative properties of samples, extinction coefficient of $k(\lambda)$ is calculated based on the amount of transmittance coefficient and

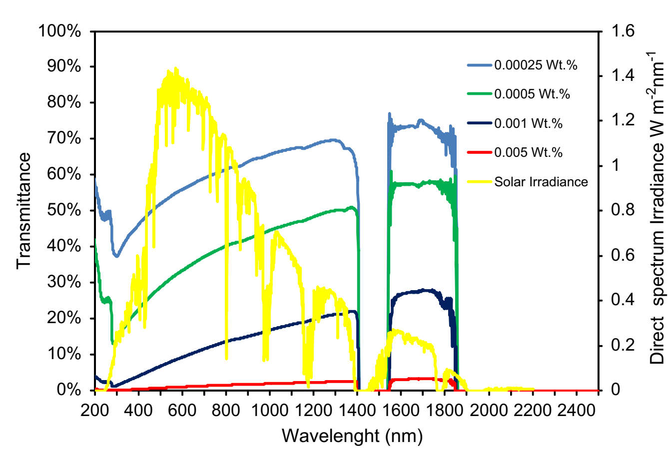


**Fig. 5.** Transmittance spectra of the samples.

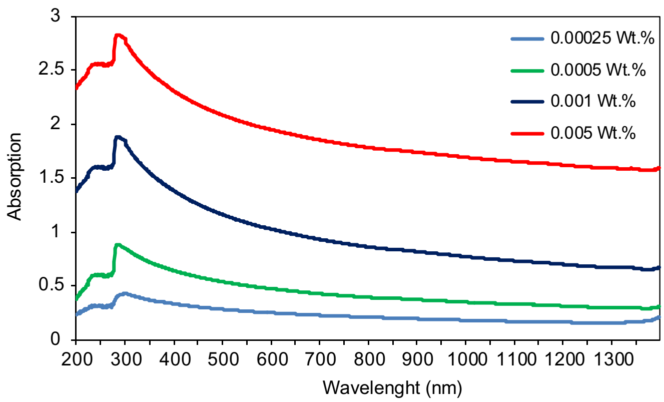


**Fig. 6.** UV–vis spectrophotometers of samples.

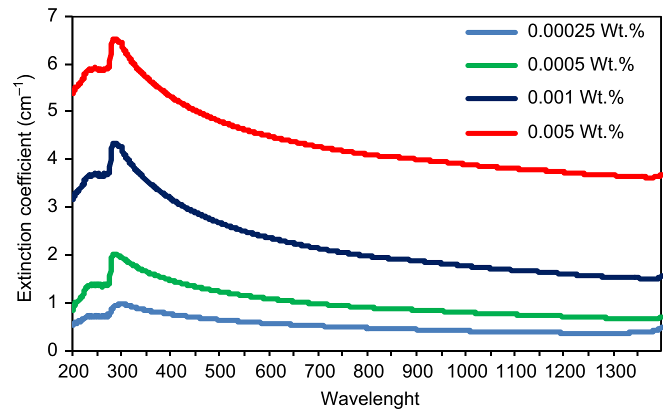


**Fig. 7.** Extinction coefficient values of samples in different wavelengths.

Bear–Lambert law, according to

$$T(\lambda) = \exp(-k(\lambda)L) \quad (2)$$

where $L$ is the length of light crossing and it is 10 mm, $T(\lambda)$ is transmittance coefficient. Nanofluids extinction coefficient with different weight percent is shown in Fig. 7. According to the results, Graphene Nanofluids with weight percent of 0.005 in the most maximum way will increase extinction coefficient up to 6.48 cm$^{-1}$.

### 3.3. The fraction of absorbed energy

Capacity of absorbed energy by nanofluid is obtained by using spectrophotometry results and extinction coefficient. By calculating the fraction of absorbed energy of $F$ and optical properties, the height and optimized weight percent of nanofluids required in direct absorption collectors can be calculated. For calculating the fraction of $F$ we use [25]:

$$F = 1 - \frac{\int_{\lambda_{max}}^{\lambda_{min}} I_{b\lambda}(\lambda)\exp(-k(\lambda)x)d\lambda}{\int_{\lambda_{max}}^{\lambda_{min}} I_{b\lambda}(\lambda)} \quad (3)$$

In this case, $x$ is equal to the thickness of the nanofluids layer which is equal to the height of fluid in direct absorption collector and $I_{b\lambda}(\lambda)$ is the solar radiation that comes from [28]:

$$I_{b\lambda}(\lambda, T) = \frac{2hc_0^2}{\lambda^5\left[\exp\left(\frac{hc_0}{\lambda K_B T_{solar}}\right) - 1\right]} \quad (4)$$

where $T_{solar}$ equals to 5800 K, $h$ is Planck's constant and $K_B$ considered as Boltzmann's constant and $c_0$ is the speed of light in vacuum. The results of the calculation of fraction of absorbed energy, $F$, according to the height of nanofluids are shown in Fig. 8.

Investigating the results show that the minimum height or thickness of the layer of nanofluids which possesses the ability to absorb solar energy completely is for nanofluids with weight percent of 0.005 with a height of 2 cm. By investigating the results we can understand that by increasing nanofluids weight percent, the amount of required height for absorbing 100 percent of solar energy will decrease. Finally, the results show that nanofluids have the potential which can be used in direct solar collector as an absorption environment. According to Eq. (4), the $F$ amount of each nanofluids samples in direct solar collector depends on two factors: extinction coefficient $k(\lambda)$ and the thickness of nanofluids layer ($x$). Increase in extinction coefficient and thickness of nanofluids layer will increase $F$ which will improve direct solar energy collector's performance. Extinction coefficient depends on several factors including the type of nano-materials and weight percent. The thickness of nanofluids layer is different on the basis of nanofluids optical properties. Hence by determining effective factor and investigating their properties, we can calculate the height and optimized weight percent in direct absorption collector by checking $F$ fraction. For determining the optimized height, we increase nanofluids weight percent so that $F$ reaches to its perfect status which is 100. Also by considering the amount of 100 for $F$, the minimum thickness layer of nanofluids will be chosen in order to increase collector performance.

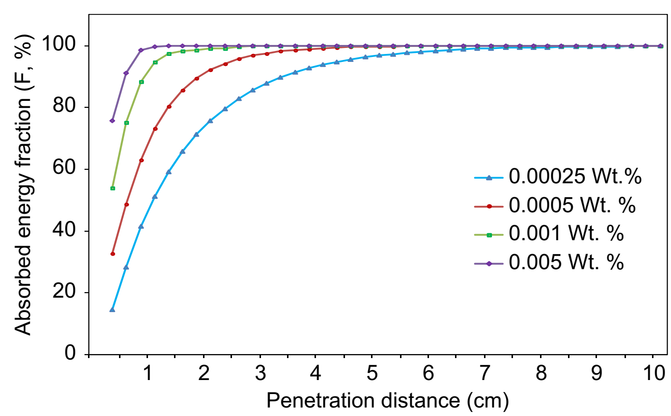


**Fig. 8.** Absorbed energy fractions ($F$) versus the penetration distance ($X$) for the nanofluids at different wt%.

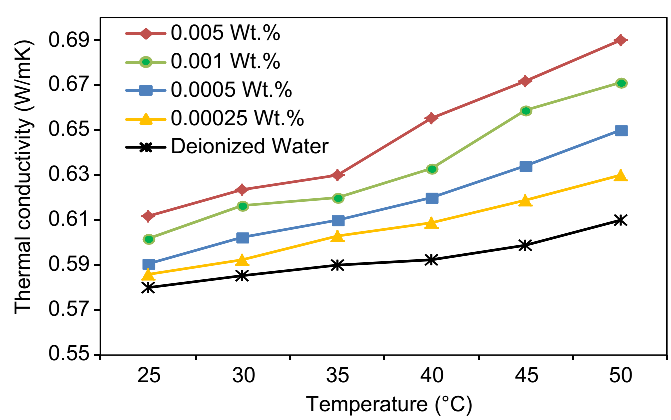


**Fig. 9.** Thermal conductivity of nanofluid samples and deionized water at different temperatures.

### 3.4. Thermal conductivity

Hence nanoparticles have more contact than microparticles and other big particles and because increased level of contact will

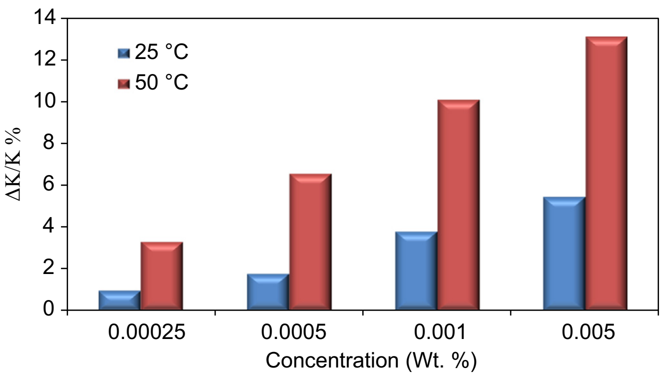


**Fig. 10.** thermal conductivity ratios of nanofluids with different wt% at 25 and 50 °C.

increase effective surface of thermal conductivity, in this part we investigate the importance of increase in nanofluids weight percent compared to increase in temperature than thermal conductivity coefficient. Results from experimental measurement are shown in Fig. 9.

As shown in Fig. 9, thermal conductivity depends on temperature which means by increasing temperature of nanofluid, thermal conductivity will increase too. Among the reasons for this dependency on temperature we can point to the very motion of nanoparticles with an increase in temperature which is due to the phenomenon of Brownian motion. Base fluid viscosity decreases with increasing temperature and Brown or scrambled movement of nanoparticles increases. The morphology of nanoparticles used in this study is in plate form so these plates are like bridges for heat transfer and by increasing nanofluids weight percent, the amount of thermal conductivity coefficient will increase either. The amount of thermal conductivity coefficient at 25 and 50 °C based on the weight of nanofluids are shown in Fig. 10.

As you can see in Fig. 10, by increasing weight percent, the amount of increased thermal conductivity coefficient at high temperatures is more visible than low temperatures. The reason, apart from increasing thermal conductivity coefficient of basic nanofluid with temperature, is that by increasing temperature of nanofluids, thermal conductivity coefficient will increase too.

## 4. Conclusion

Due to the importance of using nanofluids as an ideal environment for absorbing solar radiation, in present work, optical and thermal conductivity properties of graphene nanoplatelets are investigated as the working fluid for low-temperature in DSAC application. The nanofluids of GNPs prepared by ultrasonication were stable for a long period of time. The result of investigation showed the nanoparticles dispersed well and that nanofluids have good stability. Visual investigation showed that samples were stable without any shake and periodically agitated to 45 days without any sedimentation. Optical absorption and transmittance have been studied as a function of concentration of nanoparticles, and it is observed that the absorption increases with the increase in weight percent and transmittance decreases. Among nanofluids with different weight percent, nanofluids with weight percent 0.005 are able to absorb solar energy completely and this happens in 286 wavelength which is equal to 2.83. Increase in nanofluids weight percent reduces collector height in direct absorption collectors so that nanofluids with weight percent 0.005 and 0.00025 are able to absorb solar energy in order of 2 cm and 10 cm height. It was concluded that an increase in graphene nanoplatelets weight percent increase both the absorption coefficient and conductivity of the nanofluid. This will enhance the performance of direct absorption solar collectors.

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