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CHARACTERIZATION OF HYBRID ZnO-Ag₂O/WATER-ETHYLENE GLYCOL NANOFLUIDS FOR DIRECT PHOTOTHERMAL CONVERSION

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Abstract. *The present work experimentally investigated the absorbance spectrum of hybrid ZnO-Ag₂O/H₂O-EG nanofluids and its thermal conductivity and viscosity for future use as photothermal conversion medium in a direct absorption solar collector (DASC). The hybrid nanoparticle was obtained by the method of coprecipitation, varying the Ag₂O concentration, resulting in 11 different hybrid nanofluids samples. The XRD (X-Ray diffraction) technique was used in order to determinate nanoparticles crystalline structure and mean size. The nanofluids (0.5 wt% concentration) were prepared using a two-step method with the addition of nanoparticles (powder sample) in a mixture of water and ethylene-glycol (50:50) and the dispersion was obtained through ultrasonic vibration. Thermal conductivity and viscosity measurements were taken in the temperature range of 10°C to 40°C. The absorbance measurements showed that doping ZnO nanoparticles with Ag₂O causes an absorbance increase for the nanofluids samples with doping silver concentrations between 0.1 and 3%, with decay for the samples doped with higher Ag₂O concentrations. The thermal conductivity of the ZnO:5Ag sample presented an increase of 10% at 40°C and the temperature rise resulted in viscosity reduction for all samples. The study showed that hybrid ZnO-Ag/H₂O-EG nanofluids could be great candidates for using as photothermal conversion medium since they have higher absorbance than pure Ag₂O/H₂O-EG and ZnO/H₂O-EG nanofluids. The results also suggest that there is an optimal Ag₂O concentration for doping ZnO nanoparticles for better results, and, for wavelengths between 600 and 800 nm, the doping process reaches the best absorbance with a concentration of 3% Ag.*

Keywords: nanofluids, hybrid nanoparticles, characterization, optical properties, DASC.

1. INTRODUCTION

In the last two decades, research has focused on the increase of thermal conductivity of traditional refrigerant fluids with the addition of nanoparticles. As a result, it was obtained colloidal dispersions of solid particles (metals, oxides or carbon-based materials) in nanoscale range in liquids (water, ethylene-glycol, oils, etc) called nanofluid. The first researcher to mention this new class of fluid was Choi in 1995.

Among the applications of nanofluids, its use as photothermal conversion medium is been highly reported in the literature (He et al., 2011; Yousefi et al., 2012; Liu et al., 2013; Bandarra Filho et al., 2014; Tong et al., 2015; Vincely and Natarajan, 2016; Chen et al. 2017; Duan et al., 2018). Although many studies showed an increased interest just in the past years, the use of nanoparticles dispersions for solar radiation absorption is dated from the end of the 70's decade (Minardi and Chuang, 1975). In this context, the present focus is on the research of methods that could increase photothermal conversion efficiency of devices using nanofluids. Trying to reach maximum efficiency, the use of hybrid nanoparticles and hybrids nanofluids for photothermal conversion applications has been explored (Lenert and Wang, 2012; Fu et al, 2017, Duan et al, 2018).

The synthesis and characterization of semiconductor oxides, among which is ZnO, has attracted attention due to its use as a component in electronic, optical and electrochemical devices produced in nanoscale (Chen and Lo, 2011). One of the attractive characteristics of semiconductors as ZnO is its wide band gap, what makes possible the properties modification by the insertion of a transition metal ion in its network. By inserting these metal ions into the ZnO matrix, the emission properties are changed by forming new recombination levels for the electrons (Romeiro, 2014). Doping of ZnO nanoparticles with silver (Ag⁺) ions has been prominent in the Solid-State Chemistry area, because silver shows to be a promising dopant and significantly improve the electrical and photocatalytic properties of ZnO (Amornpitoksuk et

al., 2012; Yldirim et al., 2013). Considering the use of nanofluids in solar applications, doping of ZnO with silver (Ag^+) ions is of great interest because it produces ZnO/Ag nanostructures with high light absorbance performance.

Thus, the present work investigated thermal properties and solar absorbance spectrum of hybrid nanoparticles ($\text{ZnO-Ag}_2\text{O}$) dispersed in water-EG(50:50) to elucidate the feasibility of its use in direct absorption solar collectors (DASC's - solar collectors that have a transparent cover and a working fluid that is responsible for the photothermal conversion process, instead of a selective surface).

2. EXPERIMENTAL PROCEDURE

In the present work, the hybrid nanoparticles and pure ZnO were synthesized at room temperature by the method of coprecipitation. Ag^+ ions were used as dopant varying the nominal concentration (from 0.1 to 11%), resulting in 11 different hybrid nanofluids samples, maintaining the synthesis parameters, such as time, temperature and heating rate for all samples.

The SEM images of the pure and doped ZnO samples were acquired on a Vega 3 TESCAN microscope device operated at 20 kV using a secondary electron detector. XRD patterns were measured by a Shimadzu XRD-6000 diffractometer with a Cu-target radiation ($\lambda = 0.154 \text{ nm}$). The equipments used in measurements is located in the Multi-User Laboratory (LMIQ - UFU) of the Chemistry Institute of the Federal University of Uberlândia. All characterizations were performed at room temperature.

The nanofluids have been prepared by applying the two-step method consisting in the dispersion of ZnO:Ag nanoparticles in a mixture of distilled water with ethylene glycol (50:50) for 0.5 wt% mass concentration. For dispersion and homogenization of the nanoparticles, an ultrasonicator (Hielscher Ultrasound Technology, UP100H, 100 W, 30 kHz) was used for 30 min at 100% amplitude. All of the processes were conducted at room temperature. The two-step method was aimed at the synthesis of homogeneous suspensions with long term stability, without particles agglomeration. Thermal conductivity was measured using the transient hot bridge method, equipment acquired from Linseis, model THB-1. Dynamic viscosity was measured in a cylindrical, rotational viscometer, model SVM 3000 manufactured by Anton Paar.

The absorbance was measured using the UV-VIS 1800 spectrophotometer (Shimadzu), with photometric range from -4 to +4 Abs. the procedure was conducted in two steps, the first, without any dilution of the samples, the measurements were taken just in the visible-light range (380-800nm) aiming to investigate any trend in the absorbance results considering the increase of Ag_2O concentration used in each doping process, and, the second one, with the dilution of each sample until the results fits the photometric range of the equipment to verify the hybrid characteristic of the absorption peak for different samples.

3. RESULTS AND DISCUSSION

The X-ray diffractometer (XRD) was used to confirm the formation of hybrid nanoparticles and to determine the structure of the crystal and the mean size. Fig. 1 shows the XRD patterns of the synthesized samples. It was observed in all XRD patterns, thin diffraction peaks, confirming the formation of crystalline nanoparticles. The diffraction characteristics of ZnO and Ag_2O showed sizes of 28 and 30 nm, respectively.

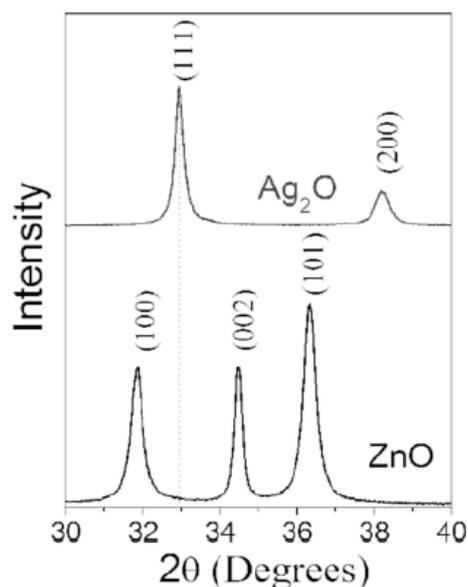


Figure 1. XRD patterns of synthesized ZnO:Ag₂O and Ag₂O samples.

Fig. 2 shows the SEM images of selected samples (Ag_2O , ZnO, ZnO:0.3Ag, ZnO:3Ag and ZnO:9Ag), confirming the shaped Ag-doped ZnO nanocrystals, as well as the spherical morphology of nanoparticles.

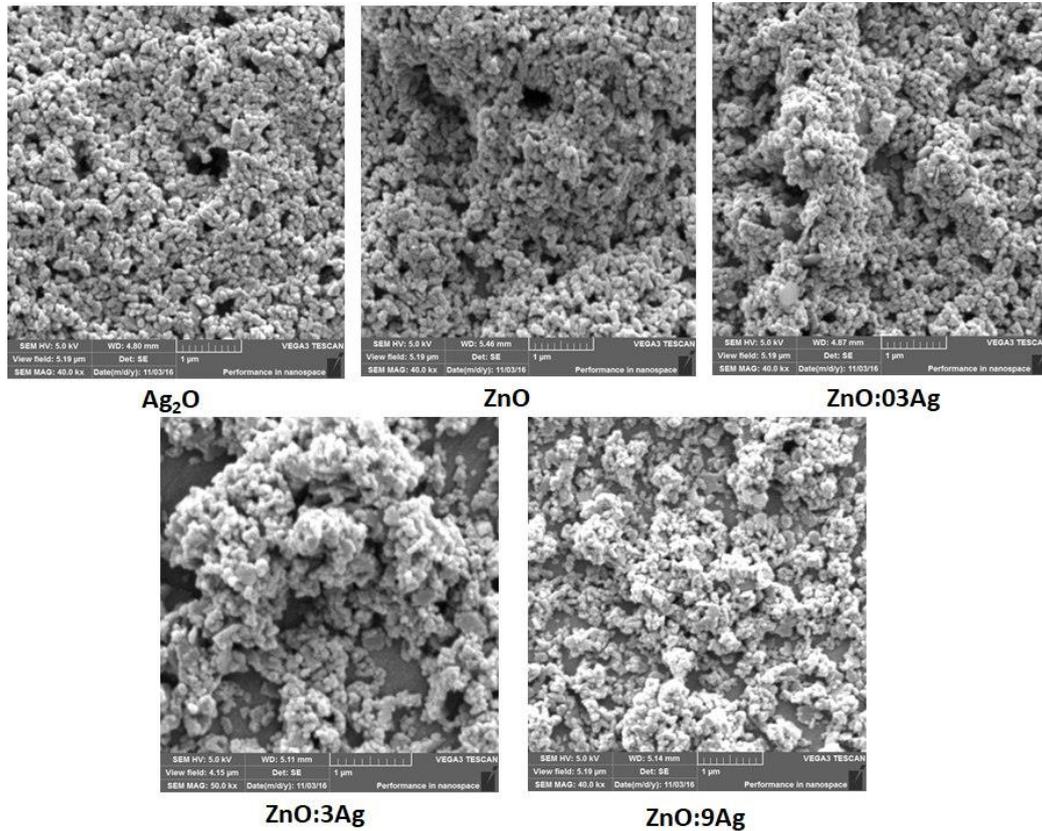
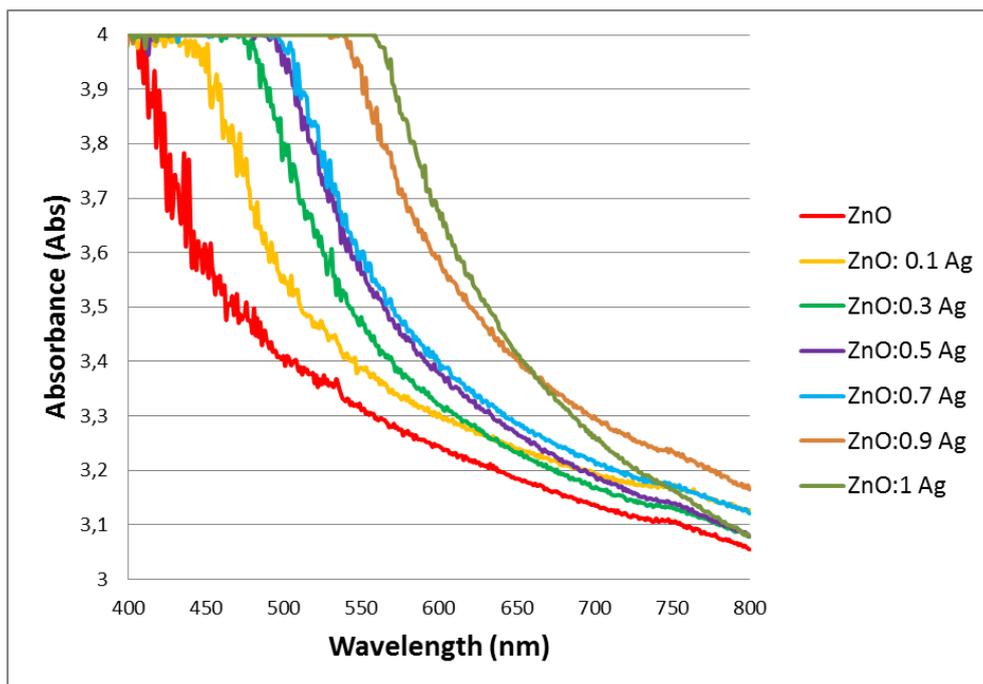
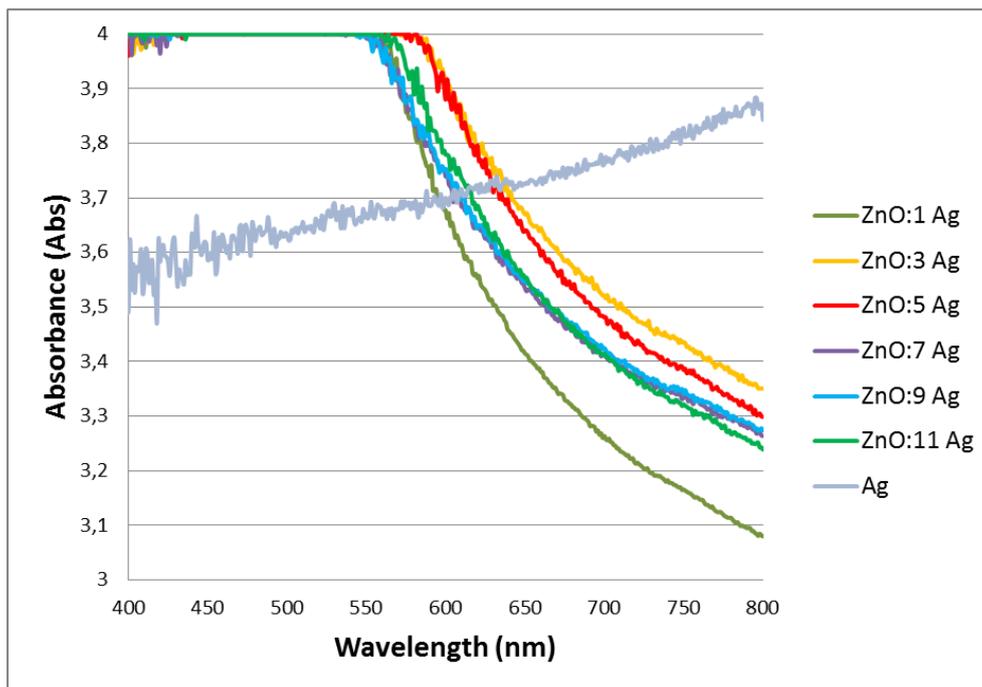


Figure 2. SEM images for different samples.

The absorbance spectrum of the samples without dilution can be seen in Fig. 3. It is noticed that some data get out of the equipment range (max. 4 Abs) for the shorter wavelengths (< 600 nm). For longer wavelengths the absorbance increased for the samples with doping silver concentrations between 0.1 and 3%, with decay for the samples doped with higher Ag_2O concentrations.



(a)



(b)

Figure 3. Absorbance spectrum in visible-light range for different nanofluids samples. (a) Pure ZnO to ZnO:1 Ag and (b) ZnO:1 Ag to pure Ag₂O.

Fig. 4 shows the absorbance spectrum of five diluted samples and it is possible to observe the progressive smoothing of the ZnO absorption peak with the addition of Ag⁺ to the crystalline structure of the semiconductor oxide, this property change is characteristic of hybrid nanoparticles (the absorbance spectrum becomes a proportional mixture of the two nanoparticles spectrum used in the synthesis).

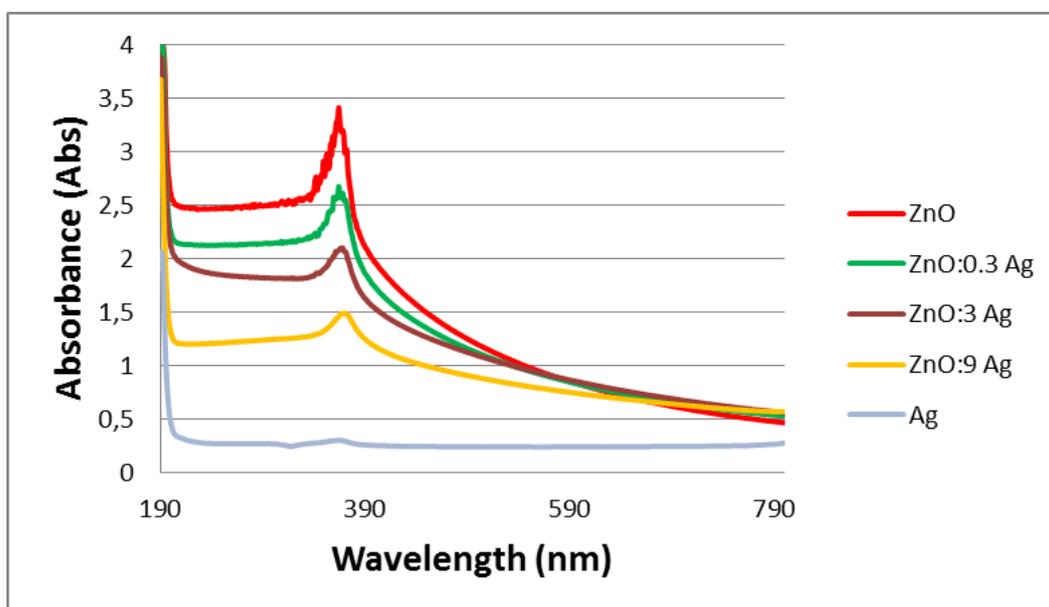


Figure 4. Absorbance spectrum in UV-vis range for different nanofluids samples.

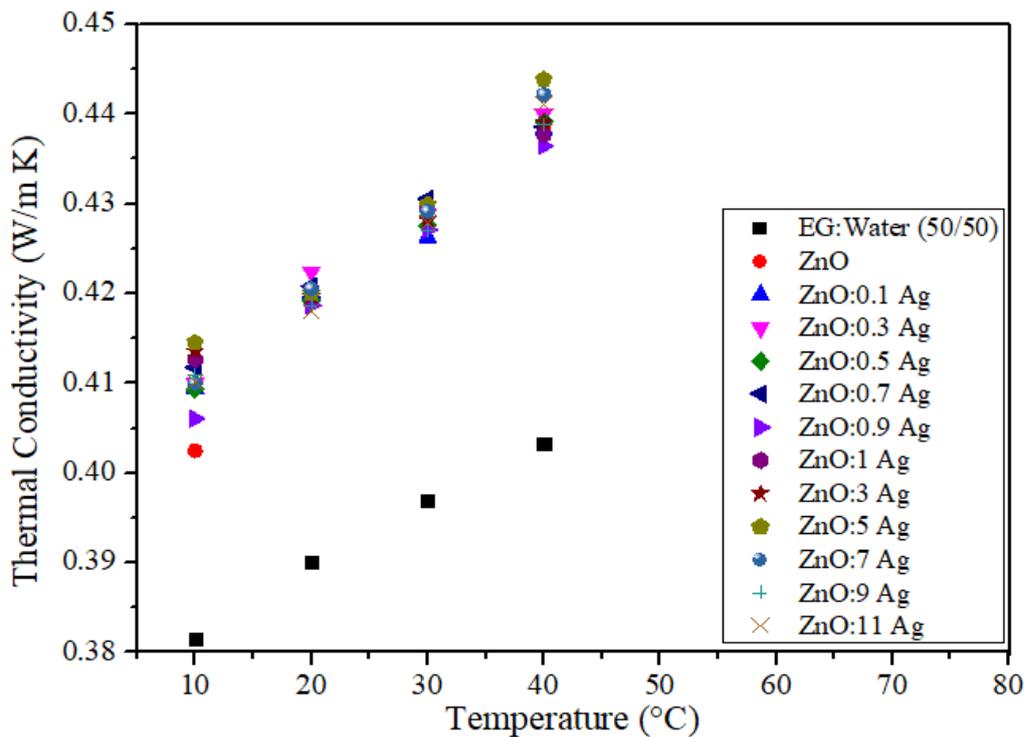
Nanofluids that contain nanoparticles which efficiently absorb solar radiation promise to overcome these difficulties in photo-thermal solar energy conversion. Notably, their superior optical and thermo-physical properties, including thermal conductivity, play a key role to enhance solar energy absorption and conversion (Potenza et al, 2017; Mehrali et al, 2018). A series of studies have been performed in order to optimize solar absorption of nanofluids, with respect to nanoparticle material, size, shape, volume fraction, etc. (Mehrali et al, 2018). In addition, the development of new nanoparticles such as hybrids has shown great potential for application in solar absorption systems. ZnO is considered a promising photocatalyst due to its non-toxicity and low cost. In addition, metal cation doping (Ag⁺) is a form of

modification of this semiconductor in order to improve its photocatalytic activity or to prolong its light absorption in the visible region. There are already studies in the literature exploring the photocatalytic properties of Ag⁺ ions doped ZnO such as Zhang et al (2012), Sun et al (2012) and Saravanan et al (2013).

Fig. 5 shows the results of (a) thermal conductivity and (b) viscosity for the studied nanofluids. It can be observed that all nanofluids presented higher thermal conductivity compared with the base-fluid, and the ZnO:5Ag sample presented the best result, with an increase of 10% in the thermal conductivity at 40°C. It was also noticed that the effect of temperature on thermal conductivity was stronger at higher temperatures (40°C). This trend could be explained by the increase of nanoparticle's random motion at higher temperatures, resulting in numerous collisions between the nanoparticles surface with the fluid molecules, improving the thermal conductivity.

In a similar study, Esfahani et al. (2018) examined the thermal conductivity of hybrid nanofluid of ZnO-Ag (50% – 50%)/water. They observed that the maximum value of thermal conductivity was for a volume fraction of 2% at 50 ° C, indicating a 25% increase. According to this study, the role of the Brownian motion is intensified with increasing temperature plus increasing concentration. Regarding the silver percentage in the ZnO crystal, it can be stated that the best fraction was 5% representing the sample ZnO:5Ag. An hypothesis that would explain this fact is that the ZnO crystal has saturated with the Ag⁺ ions, and any value above this already shows the formation of silver oxide (Ag₂O) on the crystal surface acting as a barrier to the thermal conductivity increase.

It is seen in Fig. 4 (b) that the temperature increase caused viscosity reduction for all samples. It occurs due to elevation in temperature that causes the breakdown of interatomic/inter-molecular forces and excites the movement of particles thus reduction in dynamic viscosity of the substance prevails accordingly. According to Shah and Ali (2019) rheological properties of the working fluid have major influence in the performance of solar energy application systems since uncontrolled variation in viscosity or density will increase the frictional effects and pumping power worsening the overall performance of the systems.



(a)

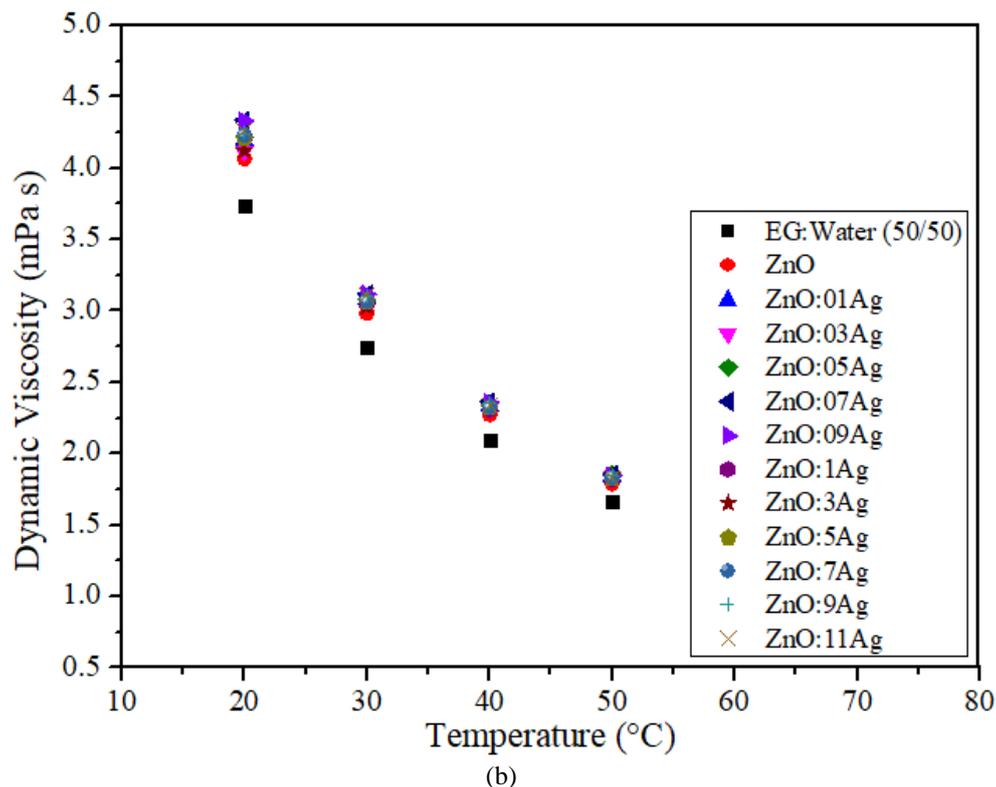


Figure 5. (a) Thermal conductivity and (b) viscosity of nanofluids.

4. CONCLUSIONS

The characterization of the samples confirmed the crystalline nanoparticle formation. The study showed that doping ZnO nanoparticles with Ag₂O caused an increase in absorbance of nanofluids in longer wavelengths (600-800 nm) for the samples with doping silver concentrations between 0.1 and 11%, with decay for the samples doped with higher Ag₂O concentrations. The ZnO:5Ag sample presented an increase of 10% in the thermal conductivity at 40°C and the temperature rise resulted in viscosity reduction for all samples. The results suggest that hybrid ZnO-Ag/H₂O-EG nanofluids could be great candidates for using as photothermal conversion medium since they have higher absorbance than pure Ag₂O/H₂O-EG and ZnO/H₂O-EG nanofluids.

5. ACKNOWLEDGEMENTS

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