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Thermal Conductivity of ZnO-CuO/DMF and ZnO-CuO/EG Nanofluids

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ABSTRACT

Mixed nanomaterials of ZnO-CuO have been synthesized using a chemical capping agentEDTA (Ethylene Diamine Tetra Acetic Acid) and a biological capping agent Aloe vera (AloeBarbadansis)by adopting the co-precipitation technique. The decomposition temperature of basic carbonate precursor for the preparation of ZnO-CuO mixed nanostructure is obtained from the thermogravimetric and differential thermal analysis. On the basis of TGA/DTA results, as prepared carbonate precursor was decomposed at 350^0C for 3 hours to obtain the ZnO-CuO mixed nanomaterials. The elemental composition of prepared nanomaterials was confirmed from EDS spectroscopy. The structural and morphological characterization of the prepared nanomaterialswere investigated usingXRD and SEM analysis. A detailed investigation of the thermal conducting properties of both EDTA and Aloe vera capped ZnO-CuO mixed nanomaterials in DMF and EG-based nanofluidswas done usingthe transient hotwire method.

INTRODUCTION

Heat transfer fluids (HTFs) play an important role in various fields such as energy conversion, thermal storage, vehicles, microelectronics, and industrial processes which require the use of coolants to prevent overheating. The major problems associated with conventional heat transfer fluids are their low thermal conductivity and heat exchange rate. The high demand for these heat transfer fluids with superior heat transfer properties has led to the development of various nanofluids.Nanofluids are novel diluted suspensions of nanometer-sized solid particles in a base fluid and are considered to be the best alternative for conventional heat transfer fluids. They show better heat transfer properties as compared to traditional heat transfer fluids such as water, oils,, and ethylene glycol. Metals with solid form exhibit higher thermal conductivity than fluids. Therefore, fluids with suspended solid particles are expected to display enhanced thermal conducting behavior than traditional heat transfer fluids, and this attracted researchers in the field of nanofluids. Several studies have revealed that the dispersed nanoparticles can increase the thermal conductivity as well as the heat transfer properties of traditional heat transfer fluids [1,2]. Metals, oxides, carbides, or carbon nanotubes are the commonly used nanoparticles to prepare nanofluids. Common base fluids include water, ethylene glycol, and oils. Solid nanoparticles suspended in energy transmission fluids can improve their thermal conductivity properties and heat transfer characteristics. Nanofluidsexhibit novel properties that can be applied in various industrial and engineering applications, such as heat exchangers, microelectronics, cooling systems in automobile and electronic equipment, fuel cells, domestic refrigerators,pharmaceutical, and chemical processes.

In recent years, several researchers performed numerical and experimental studies on nanofluids to investigate their applications to control heat transfer in different processes. Because they exhibit enhanced thermal conductivity and heat transfer properties compared to conventional base fluids. The concept of nanofluids was first introduced by Eastman and Choi in 1995 [3]. They reported that there was a 40% enhancement in thermal conductivity of ethylene glycol in the presence of 0.3 volume percent of copper nanoparticles. Nanofluids attracted more attention due to their heat transfer applications.Nowadays, the development of advanced heat transfer fluids with high thermal conductivity and improved heat transfer propertiesis in strong demand. In transportation, the efficiency of automotive and heavy-duty engine cooling rates can be improved by using suitable nanofluids. Researchers reported the effectiveness of nanofluids in industrial cooling result in great energy-saving to a large extent. Therefore, nanofluids can be considered the future of heat transfer fluids in various applications.

The presence of suspended nanoparticles in base fluids gives better thermal characteristics than conventional heal transfer fluids due to the specific surface area and stability of dispersed nanoparticles. It is possible to tune the electrical, mechanical, optical and thermal properties of nanometer-sized materials by changing their size, shape, and morphology. So, metal nanoparticles with extremely high surface-to-volume ratio are considered to have great potential in heat transfer applications. Previous researchers reported that nanofluids with small amount of metal and nonmetal oxide nanoparticles including CuO [3], Al_2O_3[4] and TiO_2[5] exhibit substantially high thermal conductivity compared to the corresponding base fluids in which they are dispersed. ZnO-based nanofluids were also found to be having applications in thermal conductivity enhancement and as car radiator coolant [6].

It has been found that thermal conductivities of nanofluids depend on several factors including size, shape, and concentration of dispersed nanoparticles, stability of dispersion, type and nature of base fluids used etc. Keblinski P et al proposed four possible mechanisms to explain the enhancement in thermal conductivity of nanofluids [7]. They are augmented heat transport by nanoparticles, Brownian motion of dispersed nanoparticles, clustering of nanomaterial, and molecular layering of liquids at the solid/liquid interface. The primary objective of the present study is to investigate the thermal conducting behavior of both chemically and biologically capped ZnO-CuO mixed nanostructures (CZE and CZA) in two different base fluids. Then the primary factors that govern the enhancement of thermal conductivity of ZnO-CuO-based nanofluids are analyzed in detail. Suspensions were prepared by mixing the appropriate quantity of ZnO-CuO mixed nanomaterial in base fluids. Here we used two base fluids to analyze the thermal conductivity of ZnO-CuO mixed nanomaterials. They are DMF (Dimethylformamide) and EG (Ethylene Glycol). These fluids possess a higher boiling point than most commonly used conventional HTF such as water.

EXPERIMENTAL

The co-precipitation method was used to synthesize ZnO-CuOmixed nanomaterialswith nearly uniform and controlled size [8].Analytical grade zinc acetate dihydrate[$(CH_3\ COO)_2\ Zn\ 2H_2O$], copper acetate monohydrate[$(CH_3\ COO)_2\ Cu\ H_2O$] and ammonium carbonate [$(NH_4)_2CO_3$] was used as the starting material for the synthesis of ZnO-CuO nanomaterial. To prevent the growth of nanomaterial during the chemical reaction, sample preparation was carried out usingEthylenediaminetetraacetic acid (EDTA) and Aloe vera Extract (Aloe Barbadansis)as capping agents. The typical method used for the preparation of ZnO-CuO nanomaterial was as follows,

For the preparation of ZnO-CuOmixed nanomaterial, 0.1 Molar Zinc Acetate, Copper Acetate, and Ammonium Carbonate were added drop by drop to a solution containing 0.01 Molar EDTA under vigorous stirring using a Magnetic Stirrer. The resultant solution was stirred for 12 h at room temperature. The obtained carbonate precursor was centrifuged, washed sequentially with distilled water and acetone several times in order to remove the unreacted ions, and then dried naturally at room temperature to obtain the carbonate precursor powder. The experiment was repeated by replacing EDTA with Aloe vera to get biologically capped ZnO-CuO nanomaterial.

In the present study,the decomposition temperature of the prepared ZnO-CuO mixed nanomaterial was identified from TGA/DTA analysis. Thermo Gravimetric Analysis of the as-prepared basic carbonate precursor precursors was taken using Perkin-Elmer diamond TGA/DTA apparatus. The weight loss and stability of the materials were observed from room temperature to 500^0C at a heating rate of 15^0C per minute under a nitrogen atmosphere.

Figure 1 shows the TGA/DTA curves of EDTA and Aloe vera capped samples.In the figure, the decomposition ofas-synthesized basic carbonate precursor started at a temperature of about 200^oC and decomposition completed at a temperature of about 300^oC producingZnO-CuOmixed nanomaterial. From the graphs, it is clear that there is a weight loss between 200^0C and 300^0C indicating the conversion of carbonate precursor to an oxide material. The small weight loss in between room temperature to 200^0C is due to the evaporation of water molecules present in the samples. Here the decomposition temperature of as prepared carbonate precursor was fixed at a temperature of 350^0C for 3 hours to obtain ZnO-CuO mixed nanomaterial.To study the temperature dependence of the structure of the ZnO-CuO nanostructure, the decomposed samples were annealed again at 500^0C and 700^0C. The list of sample codes assigned to the prepared and annealed samples are given in table 1.

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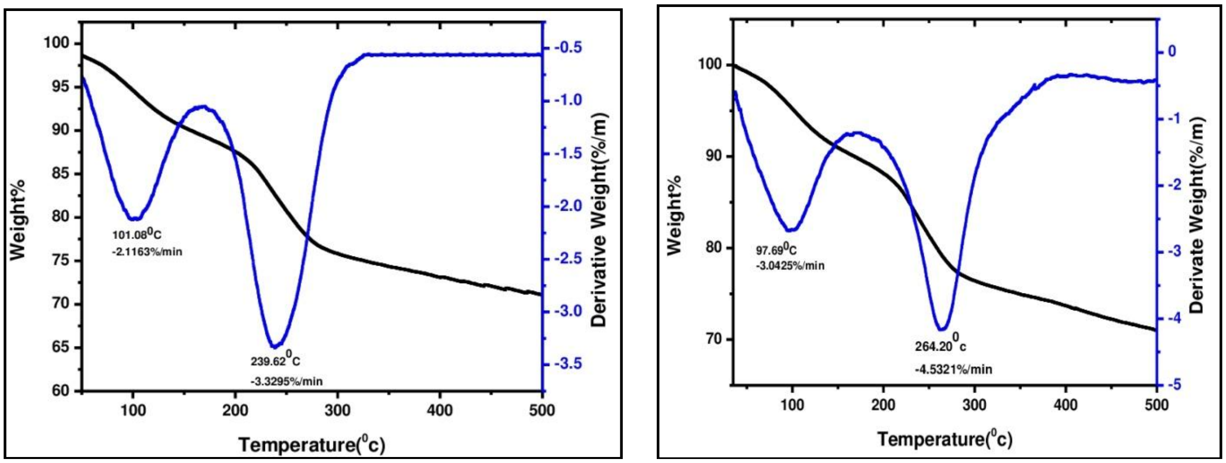


(a) **(b)**

Figure 1TGA/DTA Curves of Basic Carbonate Precursor for the Synthesis of ZnO-CuOMixed Nanomaterial using EDTA and Aloe vera as capping agents

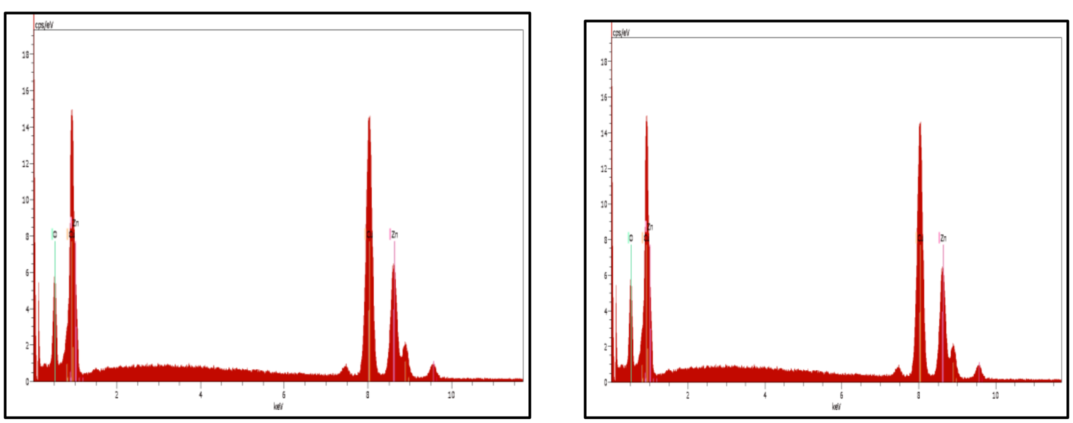
Table 1 List of Sample Codes Assigned to the Prepared and Annealed Samples

Capping Agents Used	Sample Codes		
	Prepared Samples	Annealed at 500^0C	Annealed at 700^0C
EDTA	CZE	CZE5	CZE7
Aloevera Extract	CZA	CZA5	CZA7

COMPOSITIONAL ANALYSIS

To understand the correct elemental composition and the presence of impurities if any, the EDS of ZnO-CuO mixed nanomaterial was recorded and analyzed. The EDS spectrum was recorded using the Oxford instrument swift model 7582 energy-dispersive spectrometer.

Figure 2showsthe EDS spectrum ofZnO-CuO mixed nanomaterials synthesized using Aloe vera extract aa s capping agent. As expected, the spectra clearly show the presence of zinc, copper, and oxygen indicating that all the samples wereZnO-CuO mixed nanostructures. No peaks corresponding to other materials or chemicals were found, which indicates the purity of prepared samples.



(a) **(b)**

Figure 2 EDS Spectra of ZnO-CuO Mixed Nanomaterial using EDTA and Aloe vera as Capping agents

STRUCTURAL ANALYSIS

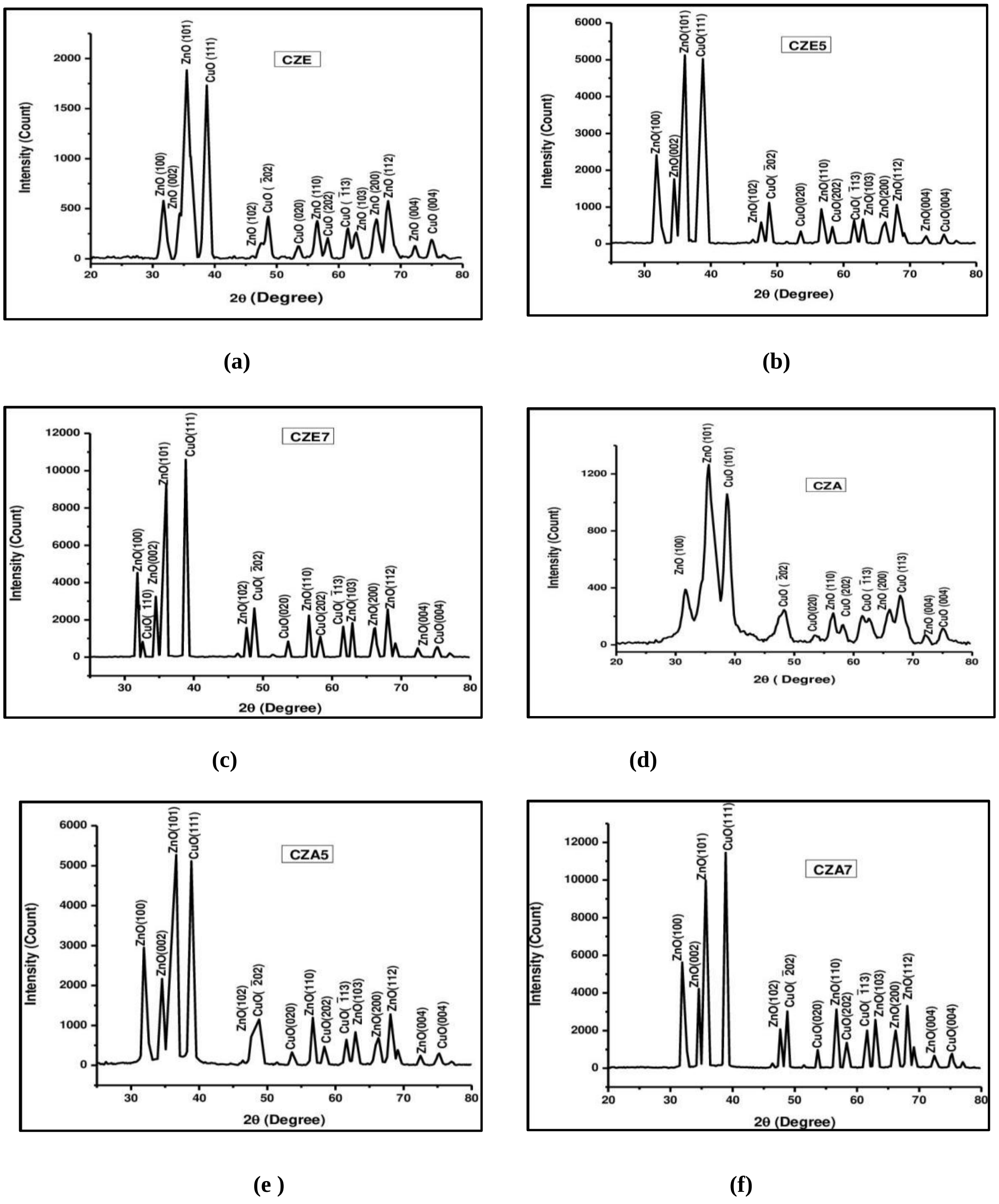


Figure 3 XRD Patterns ofZnO-CuO Mixed Nanomaterials (a) CZE, (b) CZE5, (c) CZE7, (d) CZA, (e) CZA5, (f) CZA7

The crystal structure and size of the prepared ZnO-CuO mixed nanomaterial wasconfirmed by X-ray diffraction analysis. Figures 3 shows the XRD pattern of ZnO-CuOmixed nanostructure synthesized using EDTA and Aloe vera extracts annealed at different temperatures. The formation of ZnO-CuO mixed nanostructures was confirmed from the peaks obtained in the XRD patterns. The obtained XRD patternsdisplay a pair of well-defined diffraction peaks indicating the crystalline and nanoscale nature of the prepared nanostructures. Both ZnO and CuO peaks appear in all the patterns which confirm the presence of both the materials. The diffraction peaks in the samples were in close agreement with reported values in ICDD card numbers 36-1451and 45-0937 corresponding to hexagonal ZnO and monoclinic CuO respectively. The peaks at 2θ values around 38.7^0, 48.7^0, 53.4^0, 61.8^0 and 75.0^0 belong to monoclinic CuO and peaks at 2θ values around 31.7^0, 36.2^0, 56.6^0, 66.30, 67.9^0 and 72.5^0 belongs to hexagonal ZnO [9] in all the prepared samples. The miller indices of the nanomaterials were observed as (100), (101), (111), ($\bar{2}$02), (020), (110), (202), ($\bar{1}$13), (103), (200), (112) and (004) respectively for 2θ values 31^0, 36^0, 38^0, 48^0, 53^0, 56^0, 58^0, 61^0, 62^0, 66^0, 67^0, and72^0. The bar which is indicated in the miller indices had shown the negative direction of the plane. The most intense peak of zinc oxide corresponding to the (101) plane was observed at a 2θ value of 36.1^0 and that of CuO corresponding to the (111) plane is found at a 2θ value equal to 38.7^0in all the prepared samples. The sharp, strong and intense nature of diffraction peaks in all the samples indicates the highly crystalline nature of the nanomaterial [9]. No other characteristic peaks were observed in the XRD spectra indicating the phase purity of the samples. The broadening of diffraction peaks is due to the crystalline nature of the samples.

In order to calculate the crystallite size, the full width at half maximum (FWHM) of the X-ray diffraction peak was determined. The crystallite size can be calculated by using Debye Scherer's equation,

$$\mathbf{D} = \frac{k\lambda}{\beta cos\theta} \quad \mathbf{(3.1)}$$

Where k is the shape determining factor, its value lies between 0.94 and 1.15 depending on the shape; k=1 for spherical crystallites. D is the mean diameter of the crystallites, β is the size induced line broadening (FWHM), **λ** is the X-ray wavelength and **θ** is the diffraction angle [10].

The obtained crystallite sizes of the prepared and annealed samples were given in table 2. From the XRD patterns of annealed samples, it is clear that with an increase in temperature the diffraction peaks become more intense and sharper which confirms the effect of temperature on the crystallization of samples. In addition to this, it also shows that the FWHM (Full Width at Half Maximum) decreases with an increase in temperatures, which can be attributed to the grain growth that occurs at higher temperatures. Higher temperatures stimulate the migration of grain boundaries and cause the coalescence of smaller grains to form larger grains. As a result, average crystallite size increases, when annealing temperature increases.

Table 2Average Crystallite Sizey ofZnO-CuO Mixed Nanomaterials

Sample Code	Average Crystallite Size (nm)
CZE	13±1
CZE5	25±2
CZE7	28±3
CZA	7±1
CZA5	25±2
CZA7	33±2

SEM ANALYSIS

The morphology of ZnO-CuO mixed nanomaterials was identified from Scanning electron microscopic analysis. The SEM micrographs obtained for the prepared and annealed samples of ZnO-CuO mixed nanomaterialare depicted in the figures. The obtained SEM images show that the morphology of the prepared ZnO-CuO mixed nanomaterial changes in accordance with annealing temperature. Sample annealed at 700^0C clearly shows the formation of spherically shaped particles.

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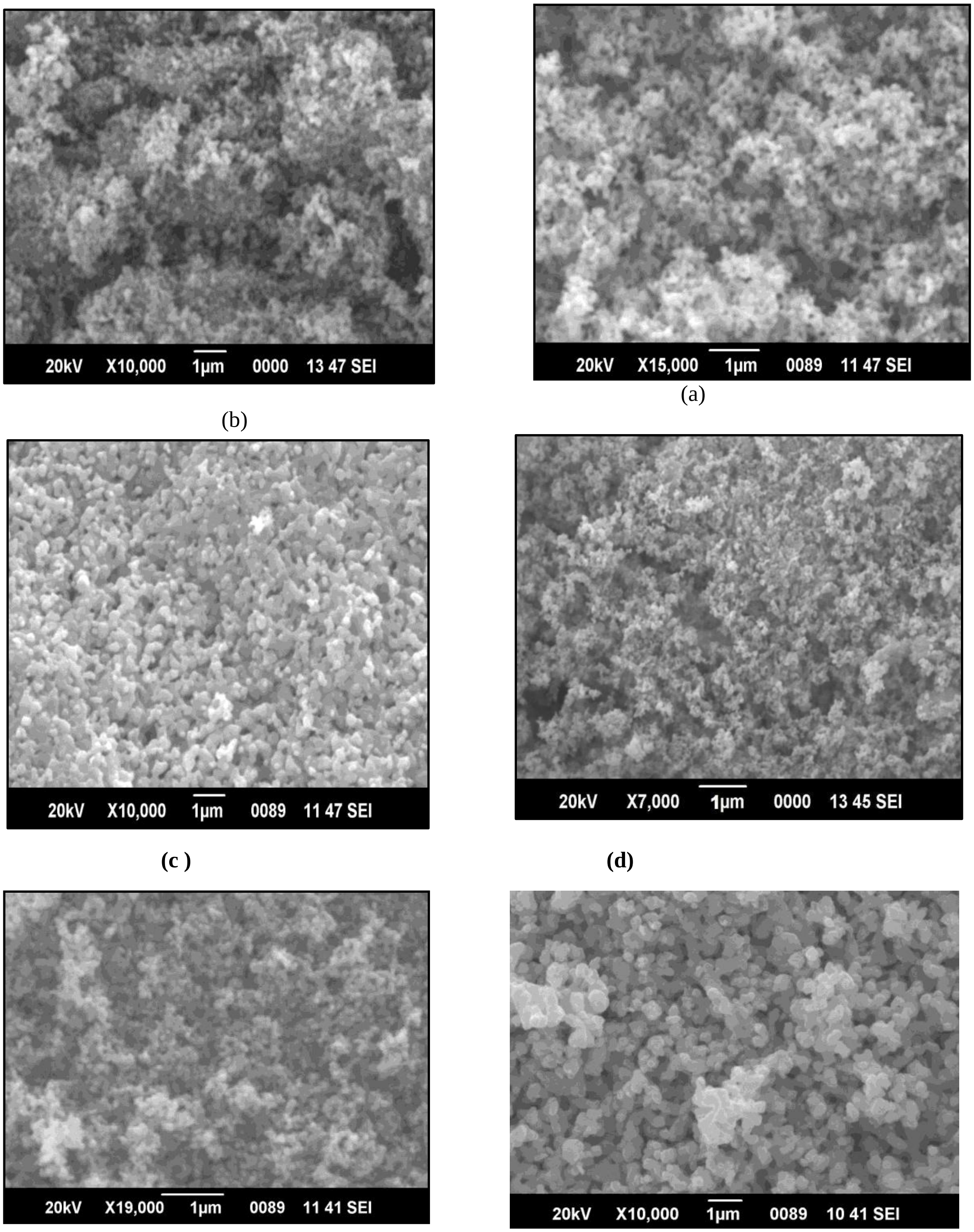


(b) (a)

(c) **(d)**

(e) **(f)**

Figure 4 SEM images of Samples (a) CZE, (b) CZE5, (c) CZE7, (d) CZA, (e) CZA5 and (f) CZA7

PREPARATION OF NANOFLUIDS

In this study, a two-step method was adopted for the preparation of nanofluids to investigate their thermal conducting behavior in the presence of ZnO-CuO mixed nanomaterial. The initial step involves the preparation of nanofluids by dispersingEDTA and Aloevera capped ZnO-CuO mixed nanomaterials (with a density around 6000 Kg/m^3) in DMF and EG by varying the nanomaterial concentration in the range 0.02 to 0.1 volume%. Then preparation of nanofluids was followed by an ultrasonication for 3 hours to attain de-agglomeration andhomogenizationof particles in the base fluid. The stable dispersion of ZnO- CuOnanomaterial in base fluids was ensured by magnetic stirring for about 30 min.The major aim of this study was to investigate the effect of concentration, size of dispersed nanomaterial, and stability of dispersionon the thermal conductivity of base fluids.Thus, the experiments were repeated with nanofluids prepared by using the synthesized and annealed samples of ZnO-CuO mixed nanostructures, CZE and CZA.

Measurement of Thermal Conductivity

During the past decade, researchers used different techniques to measure the thermal conductivity of nanofluids, which include steady state method, temperature oscillation method, hot strip method and hot wire method. Among various measurement methods, Transient Hot Wire (THW) method was considered as the simple, fastest and most widely used method for the determination of thermal conductivity. Here the enhancement of thermal conductivity of Dimethylformamide(DMF) and Ethylene glycol (EG) in the presence of ZnO-CuO mixed nanomaterial synthesized with the assistance of EDTA and Aleo vera as capping agents were investigated using the transient hot wire probe method. The KD2 Pro thermal analyzer was used for measuring the thermal conductivity of nanofluids. This instrument uses the principle of the transient hotwire technique. THW method uses the principle of calculating the transient temperature field around thehot wireby approximating that as a line source. The wire acts as a heat source and as a thermometer. The hot wire must be immersed completely into the vessel containing nanofluid. The KS1 sensor used in the experimental setup was made up of stainless steel having 60mm in length and 13mm in diameter. The sensor is placed vertically into the nanofluids. Then heat is supplied at a constant rate to measure the necessary changes in temperature. The sensor measuresthis rise in temperature depending on the thermal conductivity of the sample through which the wire is inserted. For a given applied heat input (q), the thermal conductivity of the material, k can be calculated using the Fourier's law,

$$k = \frac{q}{4\pi(T2-T1)}\ln\frac{t_2}{t_1}$$

Where, T1 and T2 are the temperatures at times t_1 and t_2, respectively. The uncertainty in the measured thermal conductivity by KD2 Pro thermal analyzer is 5 % over a temperature range of 50 to 150^0C. Figure 5 shows the schematic representation of the transient hot-wire technique for the measurement of thermal conductivity.

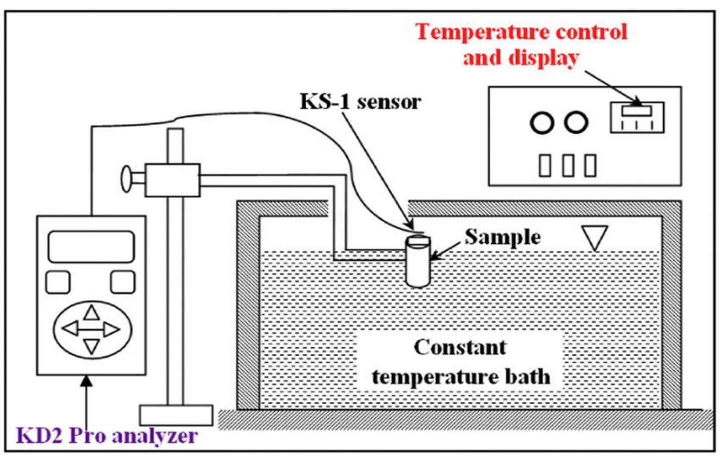


Figure 5 Schematic Representation of Transient Hot Wire MethodRef[11]

RESULTS AND DISCUSSION

Thermal conductivity measurements of five different volume percentages of ZnO-CuO mixed nanomaterial in DMF and EG based nanofluidswere done at room temperature. The effect of concentration, particle size and stability of dispersion of ZnO-CuO nanomaterial in two different base fluid such as DMF and EG were examined and reported below.

Effect of Sample Concentration on the Thermal Conductivity of ZnO-CuO Based Nanofluids

To study the effect of the concentration of ZnO-CuO mixed nanomaterials in the thermal conductivity of the base fluid, the measurements were made by changing the volume percent of CZE and CZA in base fluids from 0.02 to 0.1 Vol%.The enhancement in the thermal conductivity of ZnO-CuO-based nanofluid as a function of volumefractionof nanomaterials is shown in thefigures below.

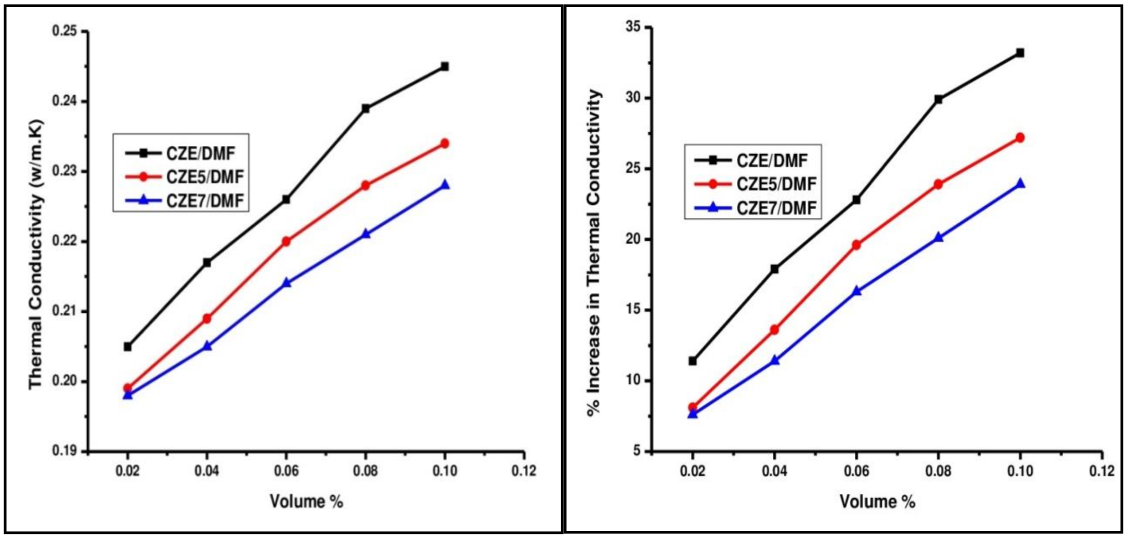


Figure 6 Thermal Conductivity of DMF Based CZE, CZE5 and CZE7 Nanofluids and the Corresponding Percentage Enhancement of Thermal conductivity as a Function of Volume Fraction

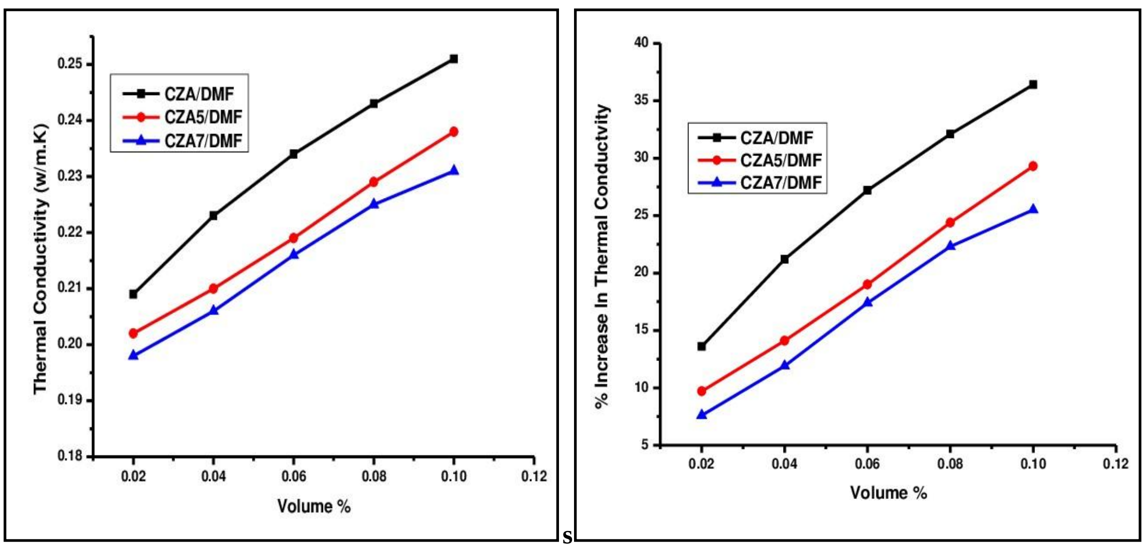


Figure 7 Thermal Conductivity of DMF Based CZA, CZA5 and CZA7 Nanofluids and the Corresponding Percentage Enhancement of Thermal conductivity as a Function of Volume Fraction

Figure 6 and 7shows the thermal conductivity values and their percentage enhancement as a function of volume fraction in DMF-based ETDA and Aloe vera-assistedZnO-CuO nanofluid. Thermal conductivity was measured by dispersing the prepared and annealed samples of ZnO-CuO mixed nanostructures in DMF by changing the nanomaterial concentration from 0.02 volume% to 0.1volume%. The obtained values of thermal conductivity and their percentage enhancement with an increase in the concentration of ZnO-CuO mixed nanomaterial in the base fluid are given in tables 3 and 4.

As observed, the thermal conductivity showed a nonlinear relationship with an increase in the concentration of ZnO-CuO mixed nanomaterials in the base fluid. Here the particle concentration was expressed as the volume fraction of nanomaterial in the base fluid. A thermalconductivity enhancement of 11.4%–33.2%, 8.1-27.2%, and 7.6-23.9% compared to pure base fluid is observed over a volume concentration ranging from0.02%–0.1% for sample codes CZE, CZE5 and CZE7 respectively in DMF based nanofluid. The percentage enhancement of thermal conductivity observedfor sample codes CZA, CZA5 and CZA7 are 13.6-36.4%, 9.7-29.3% and 7.6 -25.5% respectively when the concentration of the samples in base fluid increases from 0.02 to 0.1 volume %.

Figure 8 and 9shows the effect of volume concentration of ZnO-CuOmixed nanomaterialsof different crystallite sizes on the thermal conductivityand their percentage increment in Ethylene glycol-based nanofluid. The obtained thermal conductivity enhancement was 8.3-25.6%, 7.1-18.1%, and 6.3-16.9% respectively for sample codes CZE, CZE5 and CZE7, and it was 9.1-29.5%, 8.3-22.8%, and 6.7-17.7% respectively for sample codes CZA, CZA5 and CZA7, when the concentration of the samples in the base fluid increases from 0.02 to 0.1 volume %, and are given in table 5 and 6.

From the results obtained it is clear that, as the concentration of ZnO-CuO mixed nanomaterial in the base fluids increases, thermal conductivity also increases in both DMF and EG-based nanofluids. This is because, when the concentration of ZnO-CuO mixed nanomaterial in the base fluid increases, the distance between the particles decreases. As a result, particle to particle interaction becomes higher and this results in an enhanced thermal conductivity. Also, we can see that there is a decrease in thermal conductivity with an increase in annealing temperature. As annealing temperature increases, the size of ZnO-CuO nanomaterial in the base fluidsincreases and thermal conductivity decrease.

Table 3Variation in Thermal Conductivityof Samples in DMF Based Nanofluids

Sample Code	Particle Size(nm)	Thermal Conductivity($wm^{-1}K^{-1}$)				
		0.02 Vol%	0.04 Vol%	0.06 Vol%	0.08 Vol%	0.1 Vol%
CZE	13	0.205	0.217	0.226	0.239	0.245
CZE5	25	0.199	0.209	0.220	0.228	0.234
CZE7	28	0.198	0.205	0.214	0.221	0.228
CZA	7	0.209	0.223	0.234	0.243	0.251
CZA5	25	0.202	0.210	0.219	0.229	0.238
CZA7	33	0.198	0.206	0.216	0.225	0.231

Table 4Percentage Variation in Thermal Conductivity of Samples in DMF Based Nanofluids

Sample Code	Particle Size(nm)	Percentage Variation in Thermal Conductivity				
		0.02 Vol%	0.04 Vol%	0.06 Vol%	0.08 Vol%	0.1 Vol%
CZE	13	11.4	17.9	22.8	29.9	33.2
CZE5	25	8.1	13.6	19.6	23.9	27.2
CZE7	28	7.6	11.4	16.3	20.1	23.9
CZA	7	13.6	21.2	27.2	32.1	36.4
CZA5	25	9.7	14.1	19.0	24.4	29.3
CZA7	33	7.6	11.9	17.4	22.3	25.5

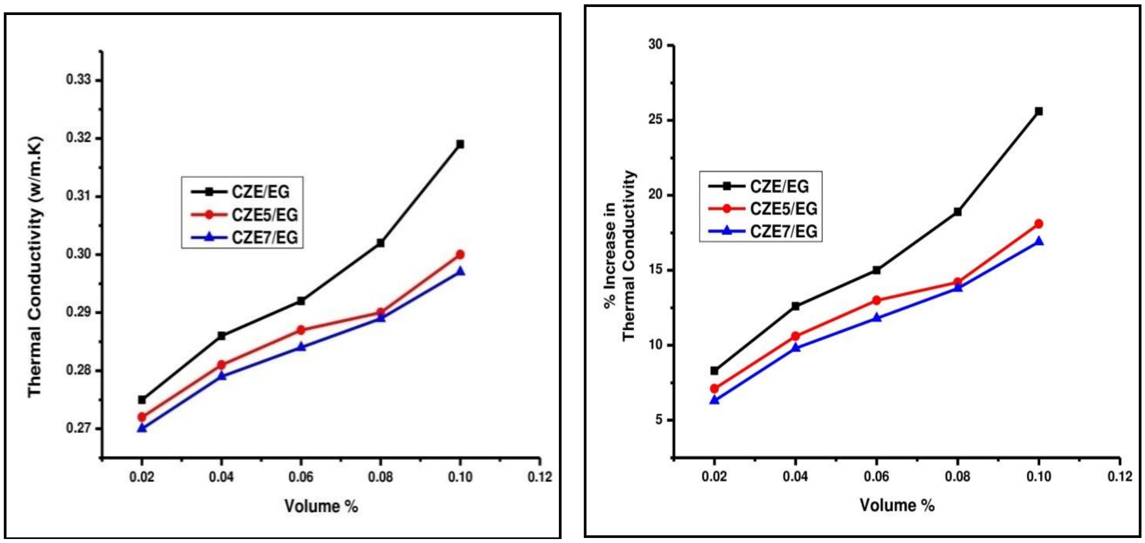


Figure 8 Thermal Conductivity of EG Based CZE, CZE5 and CZE7 Nanofluids and the Corresponding Percentage Enhancement of Thermal conductivity as a Function of Volume Fraction

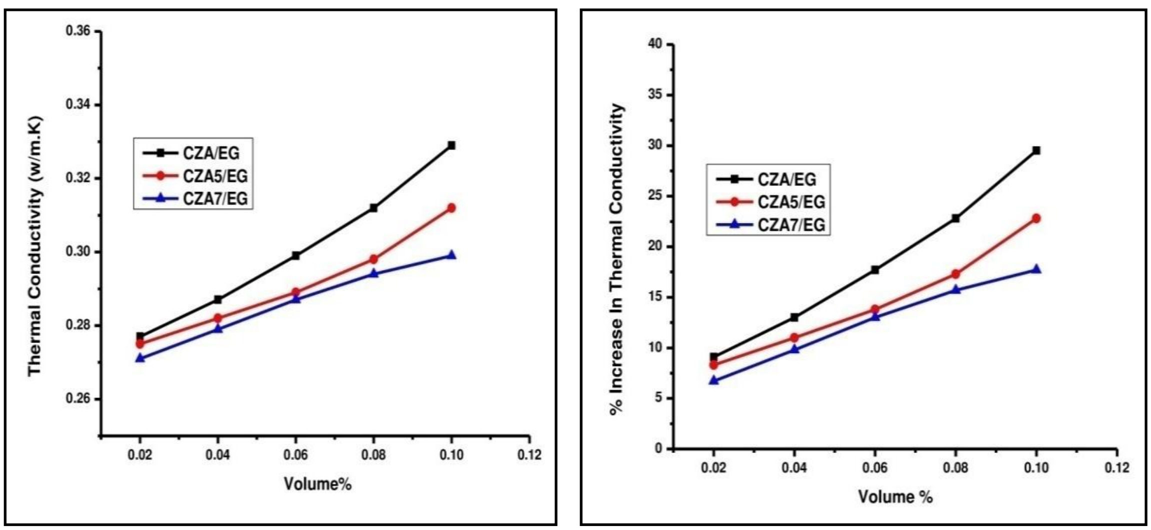


Figure 9 Thermal Conductivity of EG Based CZA, CZA5 and CZA7 Nanofluids and the Corresponding Percentage Enhancement of Thermal Conductivity as a Function of Volume Fraction

Table 5 Variation in Thermal Conductivity of Samples in EG Based Nanofluids

Sample Code	Particle Size(nm)	Thermal Conductivity($wm^{-1}K^{-1}$)				
		0.02 Vol%	0.04 Vol%	0.06 Vol%	0.08 Vol%	0.1 Vol%
CZE	13	0.275	0.286	0.292	0.302	0.319
CZE5	25	0.272	0.281	0.287	0.290	0.300
CZE7	28	0.270	0.279	0.284	0.289	0.297

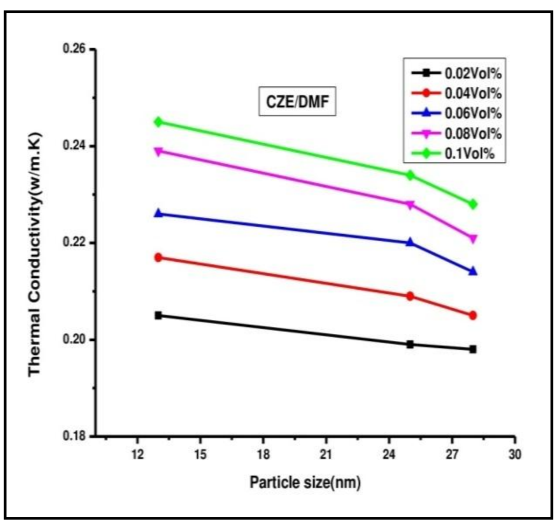
CZA	7	0.277	0.287	0.299	0.312	0.329
CZA5	25	0.275	0.282	0.289	0.298	0.312
CZA7	33	0.271	0.279	0.287	0.294	0.299

Table 6Percentage Variation in Thermal Conductivity of Samples in EG Based Nanofluids

Sample Code	Particle Size(nm)	Percentage Variation in Thermal Conductivity				
		0.02 Vol%	0.04 Vol%	0.06 Vol%	0.08 Vol%	0.1 Vol%
CZE	**13**	8.3	12.6	15.0	18.9	25.6
CZE5	**25**	7.1	10.6	13.0	14.2	18.1
CZE7	**28**	6.3	9.8	11.8	13.8	16.9
CZA	**7**	9.1	13.0	17.7	22.8	29.5
CZA5	**25**	8.3	11.0	13.8	17.3	22.8
CZA7	**33**	6.7	9.8	13.0	15.7	17.7

Effect of Particle Size on the Thermal Conductivity of Nanofluids

To analyze the effect of the average crystallite size of ZnO-CuO mixed nanomaterial on the thermal conductivity of DMF and EG-based nanofluids, the measured thermal conductivity and their percentage enhancement were plotted against particle size. Thermal conductivities and their percentage variation of CZE and CZA dispersed DMF and EG-based nanofluids as a function of nanomaterial size is shown in figure 11, 12, 13,and 14.The nanoparticles volume concentration of thedispersoids in both DMF and EG nanofluids is kept constant at 0.02-0.1volume %. The thermal conductivity is observed to decrease non-linearly with the increase in crystallite size which can be attributed to the increase in specific surface area inZnO-CuO mixed nanomaterials with the decrease in crystallite size. Also, finer particles cancarry more of the atoms on their surface, making them instantaneously available for thermalinteraction thus accelerating the heat conduction phenomenon resulting in enhanced thermal conductivity.



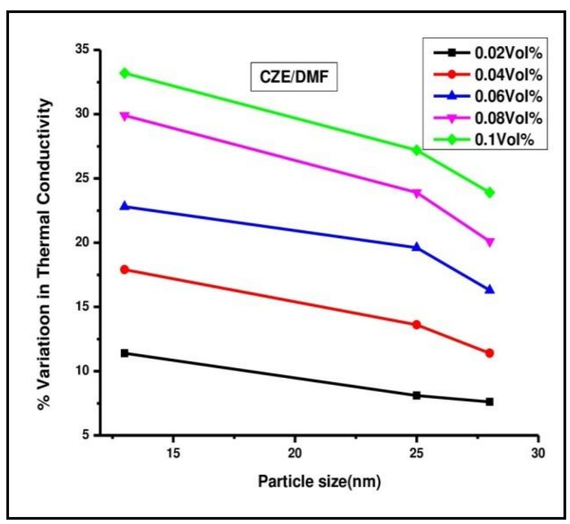


Figure 10 Variation of Thermal conductivity with Particle Size in CZE/ DMF Nanofluid

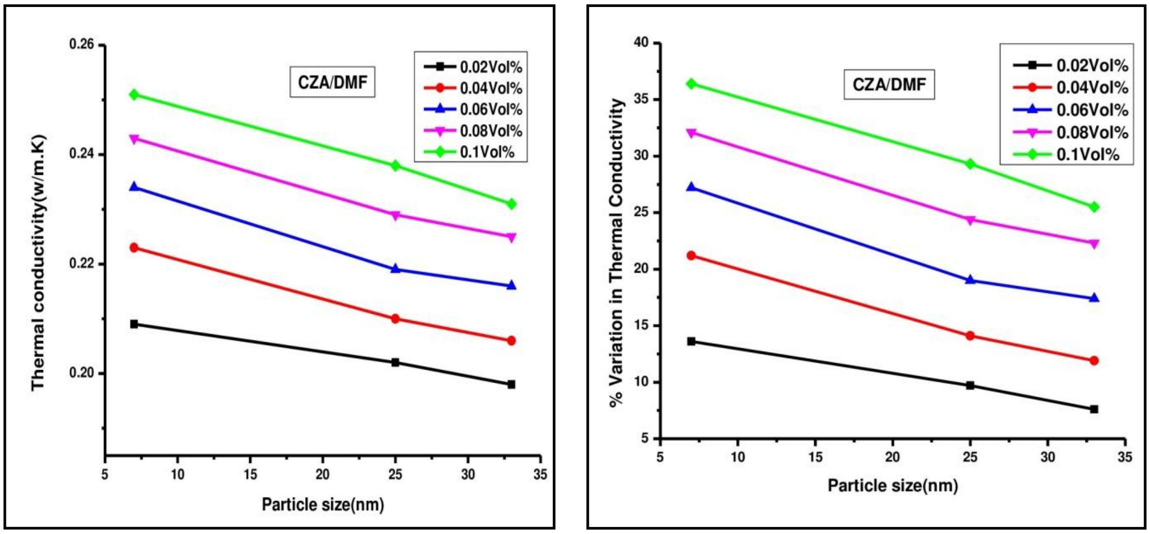


Figure 11 Variation of Thermal Conductivity with Particle Size in CZA/ DMF Nanofluid

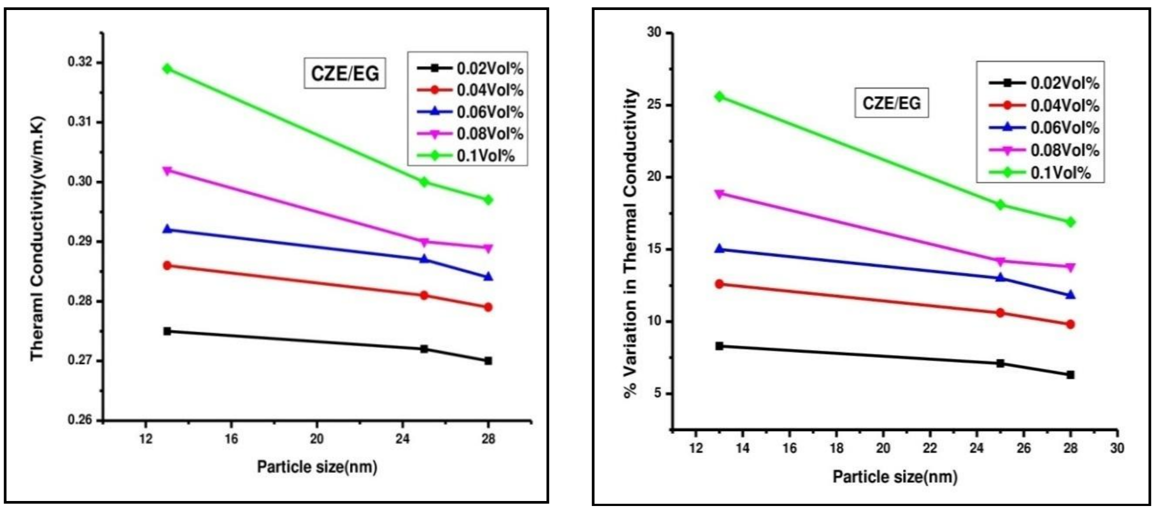


Figure 12 Variation of thermal conductivity with Particle size in CZE/ EG based nanofluids.

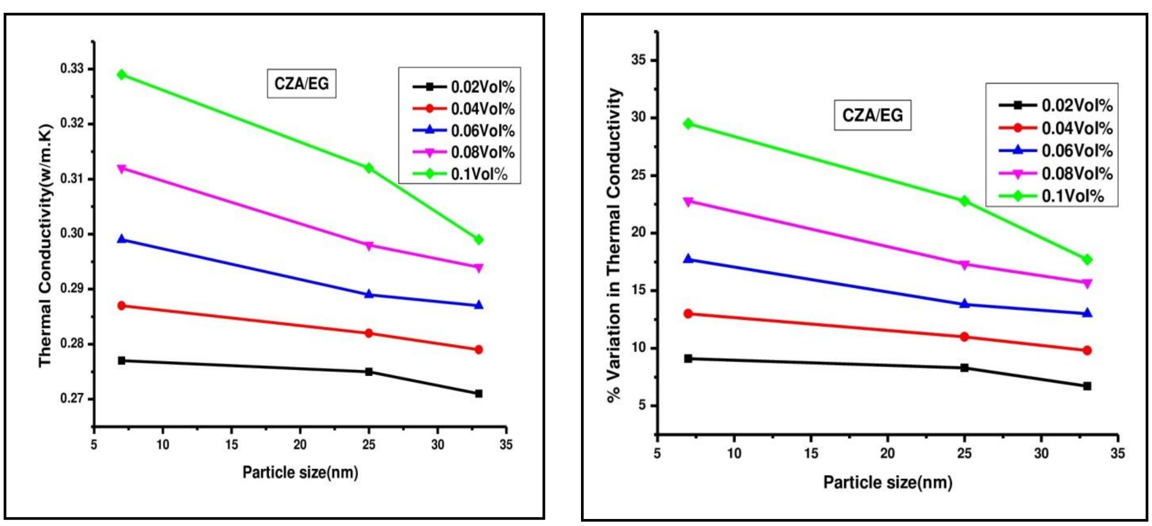


Figure 13 Variation of Thermal Conductivity with Particle Size in CZA/ EG Nanofluid

The greatest enhancement of thermal conductivity was found for ZnO-CuOnanomaterials with smaller crystalline sizes. This behavior can be explained in terms of the Brownian motion. As the particle size decreases, Brownian motion increases. As a result, smaller particles exhibit more particle-to-particle interactions, which leads to an inverse relationship between particle size and thermal conductivity.

In a solid-liquid suspension, the heat transfer occurs at the particle–fluid interface. Therefore,the increase in the surface-to-volume ratio of nanomaterials can lead to efficient heat transfer properties in nanofluids. When a nanomaterial is suspended in a liquid, they exhibit Brownian motion. As a result, the fluid molecule in the immediate vicinitycreates a locally ordered micro-convection effect around eachparticle within the base fluid. This ordered arrangement of molecules in the base fluid gives rise to an enhancement in thermal conductivity.

The addition of a nanomaterial into base fluid results in an enhancement in thermal conductivity either due to the formation of a highly ordered arrangement of liquid molecules around the particle or due to the stirring effect caused by the Brownian motion of dispersed nanoparticles. When the particle size decreases, Brownian motion increases, as a result thermal conductivity also increases. As the size of the nanomaterial dispersed in base fluid increases, there has been a tendency of particles to settle down and this gives rise to a decrease in thermal conductivity.

In comparison to CZA dispersed nanofluids, CZE dispersed nanofluids (in both DMF and EG based) exhibit lower enhancement in thermal conductivity at the same volume % of nanomaterial concentration. The experimental results show a strong size dependence onthe thermal conductivity ofnanofluids. As the average crystallite size of CZEwas larger compared to CZA nanomaterial, it exhibits a lower enhancement in thermal conductivity. From the figure, it can be seen that the size of the nanomaterial has a direct influence on the thermal conductivityof the respective nanofluids. This variation of thermal conductivity with particle size in CZE/DMF, CZE/EG, CZA/DMF, and CZA/EG nanofluids can be seen in the figure.

Effect of Stability of Dispersion on the Thermal Conductivity of ZnO-CuO Based Nanofluids

The stability of dispersion is one of the major concerns and challenges related to the commercialization of nanofluids. The stability of dispersed nanomaterial in the base fluidswasinvestigated by measuring the thermal conductivity of nanofluids at regular intervals over a period of 45 minutes. Measurements were done by dispersing 0.02 Vol% of both chemically and biologically cappedZnO-CuOmixed nanomaterials in DMF and EG.Then the thermal conductivity of the prepared nanofluids has been measured every 5 minutes up to a total duration of 45 minutes.Figure 14 and 15 shows the variation of thermal conductivity of ZnO-CuO-based nanofluids as a function of time.From the figure, we can see that fluctuations in thermal conductivity valuesexistduring the entire time duration. It has been observed that the thermal conductivity decreases with the elapse of time.

Initially, the effective thermal conductivity of CZE/DMF nanofluid was measured as 0.205 $wm^{-1}K^{-1}$and it was found to be decreased when the time elapsed and reaches 0.192 $wm^{-1}K^{-1}$ over a period of 45 minutes. In CZA/DMF nanofluid, the thermal conductivity decreases from 0.209 $wm^{-1}K^{-1}$ to 0.198$wm^{-1}K^{-1}$ after 45 minutes. The fluctuation in thermal conductivity may be attributed to their tendency to settle after a certain period of time. The percentage decrease of thermal conductivity after 45 minutes was observed to be 6.3% and 5.2% respectively for samples CZE and CZA when it is dispersed in DMF. An initial thermal conductivity of 0.275$wm^{-1}K^{-1}$ and 0.277 $wm^{-1}K^{-1}$ were observed for CZE/EG and CZA/EG nanofluids and it becomes 0.256$wm^{-1}K^{-1}$ and 0.260$wm^{-1}K^{-1}$, when it was measured after a time period of 45 minutes and the corresponding percentage decrease was observed as 6.9% and 6.1%.

From figure 6.9, it was clear that the thermal conductivity of CZA dispersed DMF based nanofluids remains unchanged up to the duration of 15 minutes and then varies slightly from the initial value when time elapsed. The observed variation in thermal conductivity was more in EG based nanofluid as compared to DMF based nanofluid.Therefore, DMF can be considered as the best dispersing medium to study the thermal conducting properties of ZnO-CuO mixed nanomaterials.

From the time dependent characteristics, it is also found that the sample CZA/DMF and CZA/EG nanofluids can be considered to be relatively stable with time in comparison with CZE/DMF and CZE/EG in both the nanofluids. Thevariation in stability arises due to the variation in particle size and formation of clusters. The average crystallite size of CZA is smaller as compared to CZE, therefore the tendency for agglomeration is more in CZE as compared to CZA when time elapsed. That is the stability of dispersion strongly depends upon the size of dispersed nanoparticle in the nanofluid.

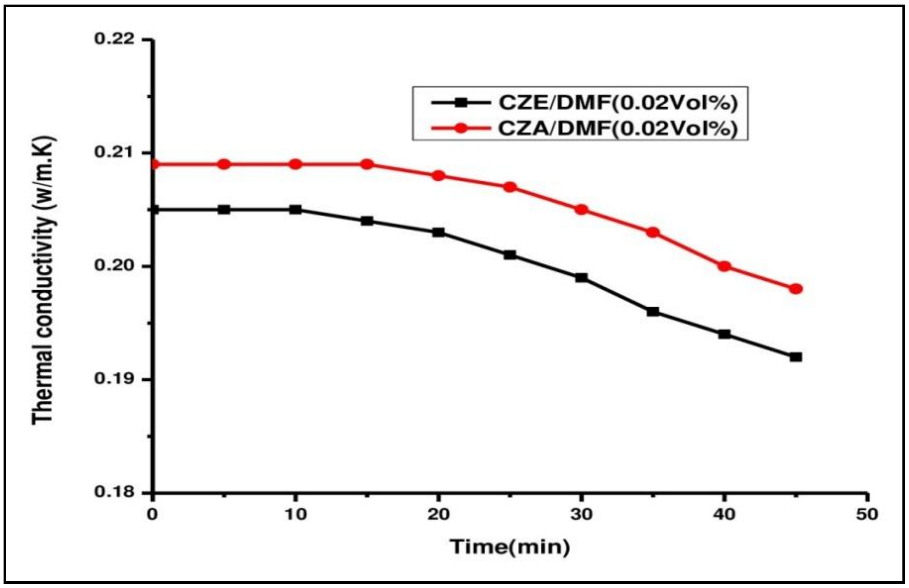


Figure 14 Variation of Thermal Conductivity with Time in 0.02 Vol% CZE/CZA/DMF Nanofluids

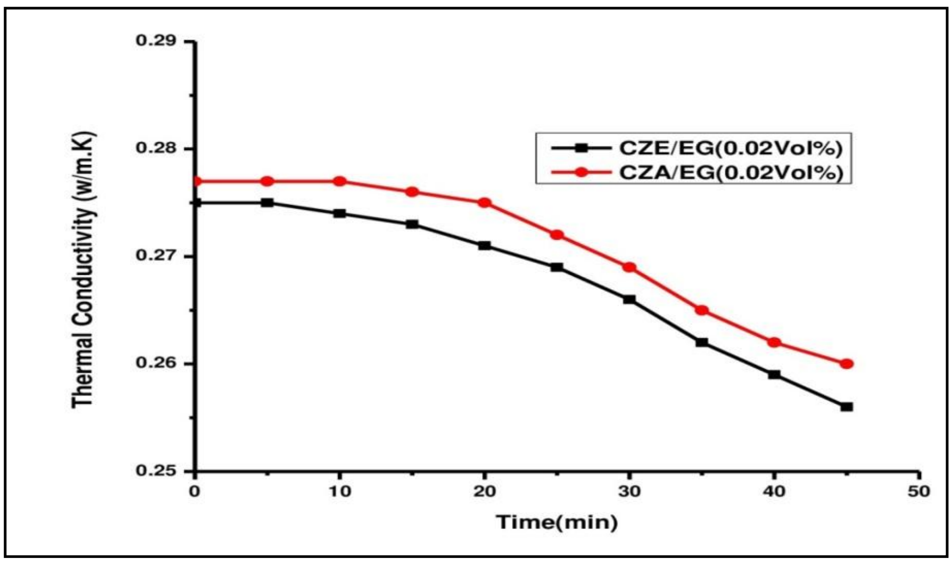


Figure 15 Variation of Thermal conductivity with Time in 0.02 Vol% CZE/CZA/EGNanofluids

From tables 3,4, 5 and 6,it is also evident that even at the same crystallite size of both CZE and CZA, the later shows a higher level of enhancement in thermal conductivity in both DMF and EG based nanofluids. This may be attributed to the fact that even though the crystallite sizes are the same, CZE form bigger clusters and exhibit larger particle sizes as compared to CZA. This trend of variation of thermal conductivity with crystallite size observed in the present study is in contradiction with the trend observed byGayatri Paul et al. Therefore, nanoparticles clustering can also be considered as an important parameter that affects the thermal conductivity of nanofluids [12]

Effect of Base fluid Type on the Thermal Conducting Properties of ZnO-CuO Mixed Nanomaterials

Figure 16 shows the comparison of percentage enhancement in thermal conductivities of CZE and CZA in DMF and EG-based nanofluids as a function of volume concentration. From the figure, it is clear that the enhancement in thermal conductivity is higher in CZE/DMF and CZA/DMF nanofluids than CZE/EG and CZA/EG nanofluids. This improvement in thermal conductivities of DMF-based nanofluids overEG-based nanofluids may be due to the higher viscosity of DMF as compared to EG. Lower viscosity fluids permit more rapid particle-to-particle interaction. As a result, more heat transfer occurs in DMF and this gives rise to a greater enhancement in thermal conductivity.

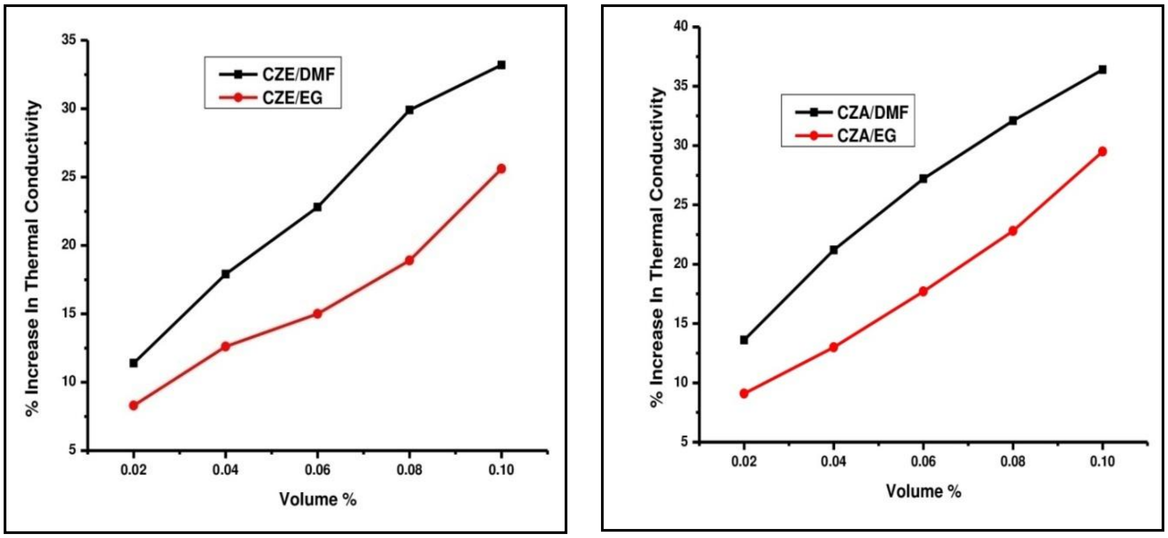


Figure 16 Percentage Enhancements in Thermal Conductivities of CZE and CZA in DMF and EG based Nanofluids

From the results obtained, it can be seen that the thermal conductivity of ZnO-CuO mixed nanomaterial dispersed nanofluids of DMF and EGare strongly dependent on factors like nanomaterial concentration, the average crystallite size of nanomaterials,and elapsed time of nanoparticle dispersion. Thus, from the study, we can conclude that the thermal conductivity of CZA dispersed DMF and EG-based nanofluids exhibited large thermal conductivity enhancement as compared to that of CZE dispersed nanofluids in terms of all the parameters such as nanoparticle concentration, size, and stability of dispersion.

CONCLUSION

Highly stable dispersions of ZnO-CuO mixed nanomaterials in DMF and EG were prepared and used as nanofluids for the measurement of thermal conductivity. In this present study, we investigated the factors which influence the thermal conductivity of prepared nanofluids. It was found that the thermal conductivity of nanofluids strongly depends on several factors such as concentration of nanoparticles in the base fluid, type of base fluid, stability of nanoparticles in the base fluid, clustering of nanomaterials in the fluid, and the average crystallite size of nanomaterials. It is found that the volume concentration of solid ZnO-CuO nanomaterial has a direct influence on the effective thermal conductivity of base fluids and it increases with an increase in concentration. There was a decrease in thermal conductivity with an increase in annealing temperature due to the increased particle size and decreased surface-to-volume ratio. Anomalous improvement in thermal conductivity with nanomaterial concentration can be accounted by any or all of the four possible mechanisms - Brownian motion of the nanoparticles, the nature of heat transport in the nanomaterials, molecular level layering of the liquid at the liquid/particle interface, and the effects of clustering. It is also found that type of base fluid and its viscosity is another important parameter that affects the thermal conductivity of nanofluids. The viscosity of base fluid inversely influences the thermal conductivity of nanofluids. These results represent an excellent initial step towards the development of ZnO-CuO nanofluids for various heat transfer applications.

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