

Research Article

Novel Nanofluid Based on Water-Loaded Delafossite CuAlO_2 Nanowires: Structural and Thermal Properties

H. Alhummiyany 

Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Correspondence should be addressed to H. Alhummiyany; halhummiyany@kau.edu.sa

Received 22 November 2017; Revised 6 March 2018; Accepted 28 March 2018; Published 8 May 2018

Academic Editor: Yuxiang Ni

Copyright © 2018 H. Alhummiyany. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ultra-high cooling performance is a crucial requirement of many thermomechanical systems, such as microelectronic devices, engine cooling systems, nuclear power systems, chemical reactors, and refrigeration systems. Recent experimental results reveal the potential thermal properties of suspended nanometallics in conventional fluids. In this study, the facile synthesis of one-dimensional delafossite CuAlO_2 nanowires by microwave hydrothermal treatment was presented. A novel type of nanofluid consisting of CuAlO_2 nanowires suspended in distilled water at various volume fractions (0.0, 0.2, 0.4, and 0.6 wt%) was successfully synthesized using an easily scalable sonication method. The microstructures of as-synthesized CuAlO_2 were investigated by adopting X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and field-emission scanning electron microscopy (FESEM). Furthermore, the thermal conductivity and specific heat capacity of water-loaded nanofluid were measured at different volume fractions and temperatures. The results reveal a significant increase in thermal conductivity with increasing CuAlO_2 loading levels and temperatures. The obtained results propound the fact that water-loaded delafossite CuAlO_2 nanowires-based nanofluid is a promising candidate for future industrial applications.

1. Introduction

Nanofluid is considered as an important material to enhance the thermal performance of any thermomechanical system [1, 2]. Nanofluids are colloidal suspensions of solid nanomaterials (sizes range from 1 to 100 nm) in base fluids [3, 4]. Recent studies reveal that nanofluids have excellent thermal properties, thermal diffusivity, thermal conductivity, viscosity, specific heat capacity, and heat transfer coefficients [5–7]. However, liquids consisting of particles manifest many issues in terms of particle deposition, blockage of flow paths, corrosion of pipelines, and low pressure [8, 9]. Recent advances in material technology allow the synthesis of innovative heat transfer fluids with enhanced transport and thermal properties by suspending nanoparticles in base fluids [9]. Generally, nanofluids possess some remarkable properties, such as less clogging problem, reduced heat transfer system size, higher thermal conductivity, better stability, and lower pressure [10, 11]. In recent years, different scientific endeavors have been carried out in the quest of new nanofluid composites with improved parameters [12]. Nanofluids can be synthesized by

either one- or two-step methods. In the one-step technique, nanoparticles and nanofluids are prepared together; hence, this route can reduce the aggregation of nanoparticles during drying, storage, transport, and dispersion of nanoparticles [8]. Therefore, it is impractical to implement the one-step technique on a wide manufacturing scale [10]. In contrast, in the two-step approach, nanoparticles and nanofluids are prepared separately. Although the area of application can be expanded by this method, the nanoparticle agglomeration, and clustering profoundly affect the strengths of nanofluids [13, 14]. Hence, finding the stability of nanofluids is a great challenge in the two-step technique. Cuprous aluminate delafossite (CuAlO_2) nanostructured has been synthesized for some time using chemical or physical routes [11, 15, 16]. Among all the techniques which have been employed to fabricate CuAlO_2 nanostructured, the water-based nanofluid loaded one-dimensional delafossite CuAlO_2 nanowire has not yet been explored deeply. The main purpose of this research was to fabricate novel nanofluid consisted of water-loaded CuAlO_2 nanowires. The microstructures of the as-synthesized CuAlO_2 nanowires were examined. Finally, the

thermal properties of fabricated nanofluids were investigated in detail.

2. Experimental Segment

2.1. Preparation of Delafossite CuAlO_2 Nanowire. All reagents (Sigma-Aldrich, St. Louis, Missouri, US) of this study were of analytical grades and used without further purification. One-dimensional delafossite CuAlO_2 nanowires were synthesized directly by reacting copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), aluminum acetate ($\text{Al}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_2$), and urea (NH_2CONH_2) under microwave hydrothermal method. The solutions were prepared by dissolving equimolar 0.7 mole of copper acetate and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) in isopropanol ($\text{C}_3\text{H}_8\text{O}$), and simultaneously, a solution of 2.5 g urea and 25 mL isopropanol was added dropwise into the aqueous solution. The as-obtained solution was stirred in a magnetic stirrer at room temperature for 60 min to yield a homogenous solution. The solution was then placed in an autoclave (100 mL Teflon-lined). The autoclave was placed in a household microwave oven and heated at 300°C for 10 min at 1200 watts. The temperature of the microwave oven was controlled with a fiber-optic temperature sensor (Model 1000, Probe LIC-2, 100574, Luxtron Corp., Mountain View, CA). All microwave treatments were operated at 3.5 GHz frequency. After the reaction, the autoclave was cooled down to room temperature. The final product, after being collected, was rinsed with deionized (DI) water followed by ethanol to avoid any agglomeration. Finally, the obtained product was oven-dried at 60°C for 24 h, and the final brownish white powder was collected for further characterization and physical tests.

2.2. Fabrication of Water-Loaded CuAlO_2 Nanowires-Based Nanofluid. CuAlO_2 nanowires with different weight percentages (0, 0.2, 0.4, and 0.6 wt%) were first dispersed in DI water to prepare a nanofluid mixture. pH of each mixture was measured and if necessary was adjusted to 4.0 ± 0.2 by adding hydrochloric acid. The mixtures were then irradiated using ultrasound (Sonics and Materials, Inc., Fibra Cell Fx 750) for 30 min to break the accumulated particles to obtain higher homogeneity. pH of the mixtures was maintained below the isoelectric point of CuAlO_2 nanoparticles (7–9 for alumina [17, 18]) to ensure positive surface charges on nanoparticles. It can be posited that surface charges on nanoparticles resulted from the reaction of hydroxyl groups ($-\text{OH}$) with H^+ of water [19].

2.3. Characterization and Measurements. The structures and phases of CuAlO_2 nanowires were measured by X-ray diffractometer (XRD, Model: Shimadzu LabXRD-5000). All measurements were taken in Bragg Brentano mode with copper anticathode $\text{CuK}\alpha$ radiation ($\lambda = 0.15405$ nm) at 20 kV and 30 mA. Diffraction patterns were recorded from 10° to 70° with a step size of 0.016° at room temperature. In addition, field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were employed to observe morphologies of synthesized nanowires. FESEM images were recorded by a JEOL JEM-2010 FEF microscope

at an acceleration voltage of 20 kV, whereas TEM images were captured using a JEOL JEM200CX device operated at 200 kV. The chemical analysis was done using EDS (Energy Dispersive X-Ray Spectrophotometer) and FESEM (Model: LEO 1530). Before taking images, CuAlO_2 specimens were covered with a 20 nm gold layer using a sputter coating unit. Thermal properties of the synthesized nanofluids were measured using KD2 Pro analyzer (Decagon Devices Incorporation, Pullman, WA, USA). The analyzer operated based on the transient hot-wire technique and consisted of sensor needles (8 mm in length and 1.5 mm in diameter). DI water was used for the calibration of KD2 analyzer. The direct digital readout recorded the values of thermal conductivities, and the obtained values were taken over the weight percentages of different filler contents at ambient temperature. Four measurements were taken for each specimen. A platinum thermocouple was used for hot wire because of its resistance over a wide temperature range. The heat capacities of nanofluids were analyzed by differential scanning calorimeter (DSC, 823, Mettler Toledo, Schwerzenbach, Switzerland). The baseline was prepared using two empty samples, and the reference curve was obtained with the help of empty pan and the pan containing reference sample. The heating was performed at temperatures ranging from 25°C to 80°C with a heating rate of $5^\circ\text{C}/\text{min}$. The dynamic viscosities of as-fabricated nanofluids were measured by a viscometer (automated ASTM D-445 viscometer system, USA) with a temperature controlled system. The dynamic viscosity measurements were recorded at steady state conditions for 15 min.

3. Results and Discussion

3.1. Morphologies and Structures of Delafossite CuAlO_2 Nanowires. The X-ray patterns of crystalline structures of delafossite CuAlO_2 nanowires are exhibited in Figure 1. The observed diffraction peaks were indexed on the basis of the standard rhombohedral structure of delafossite CuAlO_2 with $R3m$ space group (JCPDS Card number 35-1401). It can be identified that the peaks at 16.1° , 32.4° , 37.1° , 38.9° , 43.2° , 48.7° , 55.3° , 58.7° , 66.4° , and 69.1° were originated from (003), (006), (101), (012), (104), (009), (107), (013), (110), and (002) reflections planes, respectively. The absence of additional peaks in the X-ray spectrum indicates that there were no impurities in the synthesized CuAlO_2 nanowires. Moreover, intense diffraction peaks denote good crystallinity of CuAlO_2 nanostructures.

The crystallite sizes (D_{hkl}) of CuAlO_2 nanowires were estimated by Debye-Scherrer's equation [4, 20, 21]:

$$(D_{hkl}) = \frac{F\lambda}{\beta_{hkl} \cos \theta_{hkl}}, \quad (1)$$

where F represents a constant equal to 0.9, β_{hkl} represents the full width at half maximum of the (hkl) diffraction peak, θ_{hkl} represents the Bragg angle of (hkl) peak, and λ represents the wavelength of X-ray $\text{CuK}\alpha$ radiation source. The crystallite sizes (D) of the synthesized CuAlO_2 nanowires were found as 9 nm, thus confirming the nanocrystalline nature of CuAlO_2 powder.

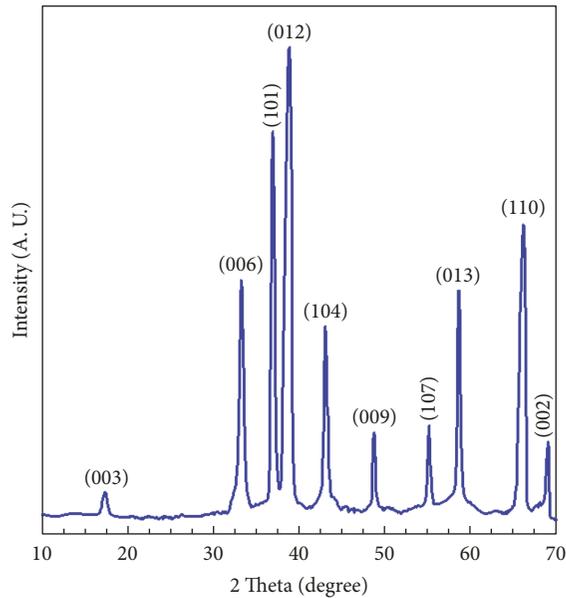


FIGURE 1: X-ray diffraction pattern of as-synthesized delafossite CuAlO_2 nanowire by hydrothermal microwave method.

The lattice parameters of CuAlO_2 nanoparticles were estimated by the following equation [1]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}, \quad (2)$$

where d represents the distance between crystalline planes and Miller indices (hkl), a and c are lattice parameters. The calculated values of a and c were found as 0.2859 nm and 1.6952 nm, respectively. It was observed that the values of calculated cell parameters (a and c) were slightly greater than that of bulk CuAlO_2 ($a = 0.2856$ nm and $c = 1.6943$ nm). This phenomenon could occur due to the influence of lattice expansion caused by the increase in oxygen vacancy and Al^3 ions with reduced particle size and increased surface relaxation during the grain growth process [4, 12].

Figure 2 displays EDS spectra of CuAlO_2 nanowires. It is evident that aluminum (Al), copper (Cu), and oxygen (O_2) were present at a suitable percentage with an atomic ratio of 1:1.35:1.70, which corresponded to the stoichiometric composition of CuAlO_2 .

Figure 3(a) presents FESEM image of CuAlO_2 nanowires. It can be noticed that nanowires were roughly distributed with a high-density packing. The lengths and diameters of CuAlO_2 nanowires were found in the range of 10–15 μm and 8–11 nm, respectively, which were consistent with X-ray results. The low-magnification TEM images of CuAlO_2 nanowires are illustrated in Figure 3(b). It is evident that CuAlO_2 nanowires possessed a clean and smooth surface with a uniform diameter of 16 nm throughout their lengths. The corresponding atomically resolved HRTEM image is presented in Figure 3(c). The distance between two adjacent planes was found about 0.27 nm, which corresponded to the d -interplanar spacing of the (012) crystal plane of CuAlO_2 . It confirmed that the fabricated CuAlO_2 nanowires were of

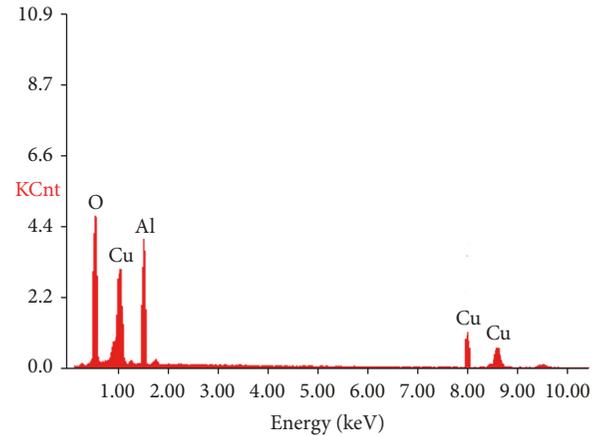


FIGURE 2: Energy Dispersive Spectroscopy (EDS) of as-synthesized delafossite CuAlO_2 nanowire.

single crystalline CuAlO_2 and synthesized along the (012) crystal plane.

The selected area electron diffraction (SAED) pattern of CuAlO_2 nanowires is shown in the inset of Figure 3(c). The SAED results were in good agreement with the observed HRTEM data.

3.2. Thermal Conductivity of Nanofluid. In order to improve heat transfer characteristics of conventional liquids, it is imperative to enhance thermal conductivities and specific heat capacities of materials [4]. Because of a greater surface area and high aspect ratio, nanomaterials behave like liquid molecules and have great potentials in heat transfer applications. Low thermal conductivities of fluids are the key limitation in promoting energy-efficient heat transfer fluids. The thermal conductivities of one-dimensional CuAlO_2 nanowires as a function of temperature at various mass fractions are plotted in Figure 4. It is evident that thermal conductivities of water-based nanofluids increased with increasing mass fractions of CuAlO_2 nanowires. The increase in thermal conductivities can be attributed to the Brownian motion of nanoparticles, the molecules at the interfacial layer, and the nanoparticle aggregation [10, 11]. The collisions between nanoparticles resulted from the Brownian motion caused heat transfer in the system. Also, the small CuAlO_2 nanoparticles behaved like liquid molecules and increased the flow of nanofluids. Another explanation is that the interaction between dynamic CuAlO_2 nanowires and water molecules enhanced heat conduction of nanofluids. It resulted in a redistribution of charge, and consequently, the entire fluid created a local convective effect at the nanoscale level and yielded an increase in thermal conductivity. To confirm the above facts, heat transfer coefficients (HTCs) and densities of nanofluids were measured as a function of mass fractions of CuAlO_2 nanowires (Figure 5). It can be noticed that heat transfer coefficients and densities were increased with increasing mass fractions of CuAlO_2 nanowires. It expounds that the inclusion of CuAlO_2 nanowires in water-based fluid enhanced the thermal stability of nanofluids due to the interaction of CuAlO_2 nanowires with water molecules.

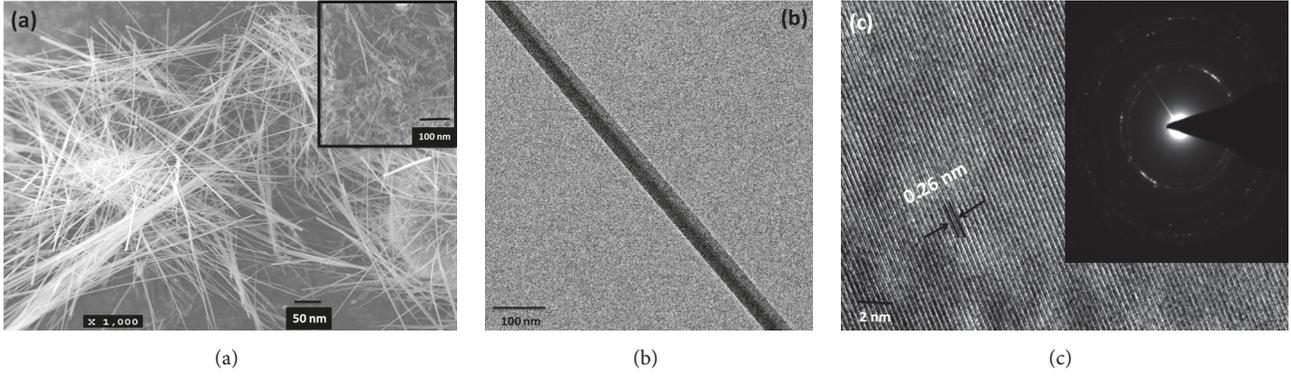


FIGURE 3: (a) Low-magnification FESEM image of the as-synthesized delafossite CuAlO_2 nanowires, (b) low-resolution TEM image of individual CuAlO_2 nanowires, and (c) the lattice-resolved TEM image of the CuAlO_2 nanowire. The inset is a SAED pattern taken along the (012) zone axis.

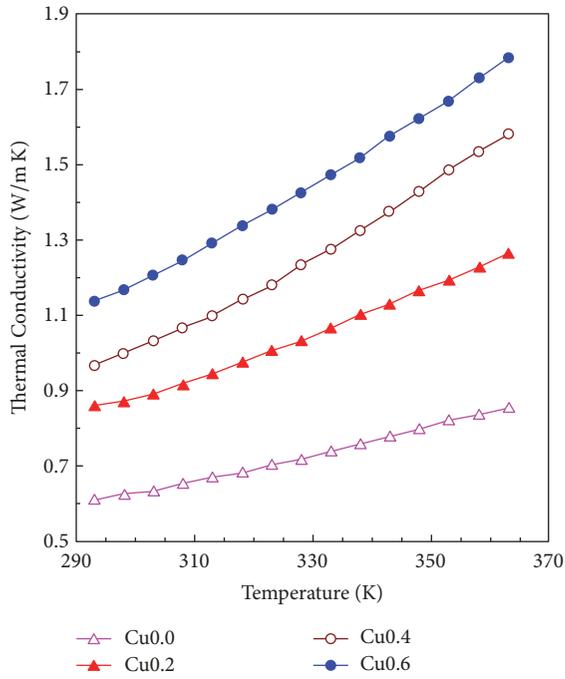


FIGURE 4: Thermal conductivity versus temperature of water-based nanofluids loaded with various mass fractions of one-dimensional CuAlO_2 nanowires.

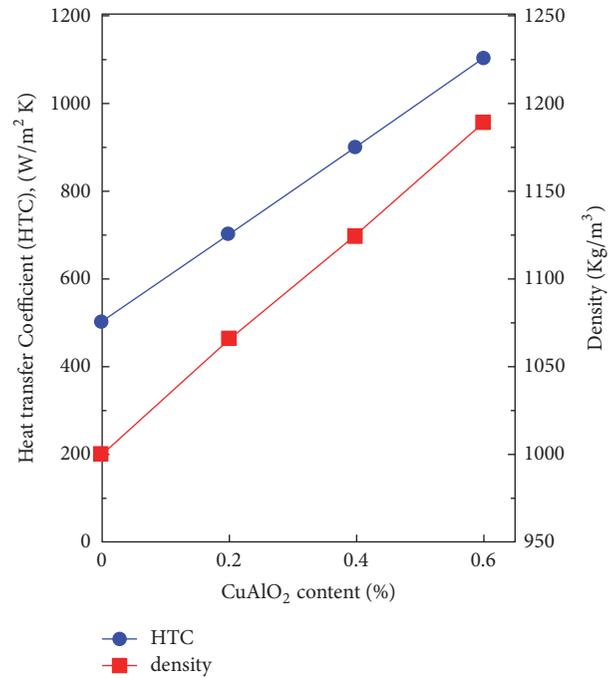


FIGURE 5: Heat transfer coefficient and density versus CuAlO_2 nanowires content in the water-based fluid.

The HTCs of nanofluids were expressed by [14]

$$\text{HTC} = \frac{kR_n^2 P_n^2}{d}, \quad (3)$$

where k is thermal conductivity, d is diameter of the nanowire, and R_n and P_n are Reynolds number and Prandtl number, respectively.

The densities of nanofluids were expressed as [10, 21]

$$\rho = \frac{k}{\alpha C_p}, \quad (4)$$

where C_p is specific heat and α is thermal diffusivity.

Reynolds number (R_n) was defined by [9]

$$R_n = \frac{\rho K_B T}{3\pi\mu^2 l}, \quad (5)$$

where K_B is the Boltzmann constant, μ is the dynamic viscosity of fluid, and l is the mean free path of base fluid molecule and was expressed as [14]

$$l = \frac{D_0}{V_R}, \quad (6)$$

where D_0 is diffusion coefficient and V_R represents velocity of nanoparticles.

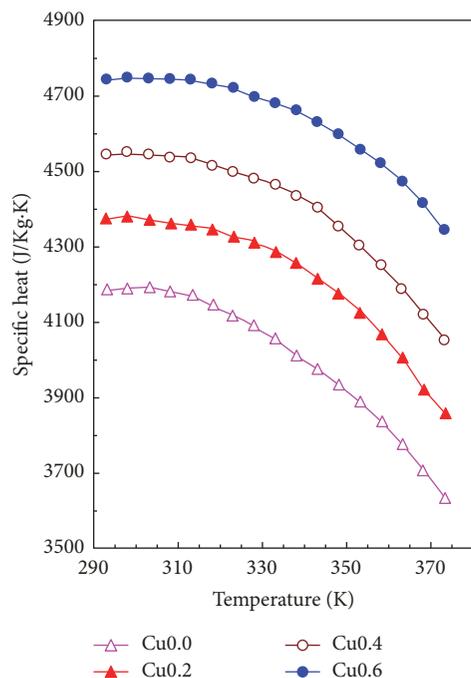


FIGURE 6: Specific heat versus temperature of water-based nanofluids loaded with various mass fractions of one-dimensional CuAlO_2 nanowires.

In fluid mechanics, Reynolds number is an important factor to predict the behavior of liquids on a larger scale [8]. These predictions can be used to measure turbulence as well as calculate the effects of scaling. The estimated values of Reynolds number as a function of the mass fraction of CuAlO_2 nanowires (0, 0.2, 0.4, and 0.6 wt%) were found as 400, 750, 1080, and 1400, respectively. It is obvious that Reynolds number increased with increasing mass fractions of CuAlO_2 nanowires. The values of Reynolds number (in the range of 300 to 1500) indicated the presence of laminar flow and transition flow regimes [10, 11]. Further, the decrease in viscosity could be ascribed to the increase in Reynolds number [22].

3.3. Specific Heat of Nanofluid. Figure 6 determines specific heat capacity values of water-loaded delafossite CuAlO_2 nanowires-based nanofluids with various volume fractions. The results explain that, with increasing mass fractions of delafossite CuAlO_2 nanowires, the values of specific heat of water-based nanofluids decreased due to the complex interaction at the solid-liquid interface formed between CuAlO_2 nanoparticles and water molecules. Furthermore, the conductivities of CuAlO_2 nanoparticles increased at the surfaces of liquid molecules because CuAlO_2 nanoparticles were highly ordered than bulk liquid molecules [13, 14]. Hence, heat conduction of nanofluids was enhanced and the thermal resistance at the solid-liquid interface was lowered as a result of the larger surface area, which was associated with smaller particles and greater fractions of ordered liquid molecules.

The interactions between CuAlO_2 nanoparticles and water molecules contributed to heat transfer of nanofluids.

It was found that, with increasing mass fractions of CuAlO_2 nanoparticles, the amount of stored thermal energy decreased [14]. Therefore, it can be inferred that a significant increase in specific heat capacity of CuAlO_2 nanofluids as compared to the base fluid provides an excellent potential for many heat extraction systems based on natural convection as the mode of heat removal.

4. Conclusion

Based on the above-discussed research, the following inferences can be drawn:

- (1) One-dimensional delafossite CuAlO_2 nanowires were successfully synthesized for the first time using microwave hydrothermal method.
- (2) XRD data revealed that the synthesized nanowires possess single delafossite CuAlO_2 structure. The results of FESEM and HRTEM confirmed that the prepared polycrystalline nanowires were quite uniform with diameters ranging from 8 to 11 nm and lengths ranging from 10 to 15 μm .
- (3) The addition of CuAlO_2 nanowires in water-based nanofluids effectively increased the thermal conductivities of nanofluids. Moreover, thermal conductivities of nanofluids were dependent on mass fractions of CuAlO_2 nanowires. Nanofluid demonstrated higher thermal conductivities at higher temperatures.
- (4) CuAlO_2 nanowires as a dopant manifested a profound effect on specific heat capacities of nanofluids.
- (5) The water-loaded CuAlO_2 nanowires-based nanofluids could provide a remarkable solution to many heat extraction systems based on natural convection as the mode of heat removal.

Conflicts of Interest

The received funding mentioned in Acknowledgments did not lead to any conflicts of interest regarding the publication of this manuscript.

Acknowledgments

This work was supported by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under Grant no. (363-122-D1439). The authors, therefore, gratefully acknowledge the DSR technical and financial support.

References

- [1] R. Saidur, K. Y. Leong, and H. A. Mohammad, "A review on applications and challenges of nanofluids," *Renewable & Sustainable Energy Reviews*, vol. 15, no. 3, pp. 1646–1668, 2011.
- [2] W. Yu and H. Xie, "A review on nanofluids: preparation, stability mechanisms, and applications," *Journal of Nanomaterials*, vol. 2012, Article ID 435873, 17 pages, 2012.
- [3] S. U. S. Choi and J. A. Eastman, *Enhancing thermal conductivity of fluids with nanoparticles*, USA, 1995.

- [4] D. Y. Tzou, "Thermal instability of nanofluids in natural convection," *International Journal of Heat and Mass Transfer*, vol. 51, no. 11-12, pp. 2967–2979, 2008.
- [5] A. Ghadimi, R. Saidur, and H. S. C. Metselaar, "A review of nanofluid stability properties and characterization in stationary conditions," *International Journal of Heat and Mass Transfer*, vol. 54, no. 17-18, pp. 4051–4068, 2011.
- [6] Y. Li, J. Zhou, S. Tung, E. Schneider, and S. Xi, "A review on development of nanofluid preparation and characterization," *Powder Technology*, vol. 196, no. 2, pp. 89–101, 2009.
- [7] T. S. Chew, R. Daik, and M. A. A. Hamid, "Thermal conductivity and specific heat capacity of dodecylbenzenesulfonic acid-doped polyaniline particles-water based nanofluid," *Polymer Journal*, vol. 7, no. 7, pp. 1221–1231, 2015.
- [8] Y. Lu, T. Nozue, N. Feng, K. Sagara, H. Yoshida, and Y. Jin, "Fabrication of thermoelectric CuAlO₂ and performance enhancement by high density," *Journal of Alloys and Compounds*, vol. 650, Article ID 35007, pp. 558–563, 2015.
- [9] J. Ahmed, C. K. Blakely, J. Prakash et al., "Scalable synthesis of delafossite CuAlO₂ nanoparticles for p-type dye-sensitized solar cells applications," *Journal of Alloys and Compounds*, vol. 591, pp. 275–279, 2014.
- [10] A. Ahmad, T. Jagadale, V. Dhas et al., "Fungus-based synthesis of chemically difficult-to-synthesize multifunctional nanoparticles of CuAlO₂," *Advanced Materials*, vol. 19, no. 20, pp. 3295–3299, 2007.
- [11] R. Mo and Y. Liu, "Synthesis and properties of delafossite CuAlO₂ nanowires," *Journal of Sol-Gel Science and Technology*, vol. 57, no. 1, pp. 16–19, 2011.
- [12] F. Al-Hazmi, F. Alnowaiser, A. A. Al-Ghamdi, M. M. Aly, R. M. Al-Tuwirqi, and F. El-Tantawy, "A new large—scale synthesis of magnesium oxide nanowires: structural and antibacterial properties," *Superlattices and Microstructures*, vol. 52, no. 2, pp. 200–209, 2012.
- [13] Y. Guo, T. Zhang, D. Zhang, and Q. Wang, "Experimental investigation of thermal and electrical conductivity of silicon oxide nanofluids in ethylene glycol/water mixture," *International Journal of Heat and Mass Transfer*, vol. 117, pp. 280–286, 2018.
- [14] S. P. Jang and S. U. S. Choi, "Role of Brownian motion in the enhanced thermal conductivity of nanofluids," *Applied Physics Letters*, vol. 84, no. 21, pp. 4316–4318, 2004.
- [15] T. V. Thu, P. D. Thanh, K. Suekuni et al., "Synthesis of delafossite CuAlO₂ p-type semiconductor with a nanoparticle-based Cu(I) acetate-loaded boehmite precursor," *Materials Research Bulletin*, vol. 46, no. 11, pp. 1819–1827, 2011.
- [16] H. Akyildiz, "Synthesis of CuAlO₂ from chemically precipitated nano-sized precursors," *Ceramics International*, vol. 41, no. 10, pp. 14108–14115, 2015.
- [17] J. Drelich, J. Laskowski, and K. L. Mittal, *Apparent and Microscopic Contact Angles*, 2000.
- [18] W. Xian-Ju and L. Xin-Fang, "Influence of pH on nanofluids' viscosity and thermal conductivity," *Chinese Physics Letters*, vol. 26, no. 5, p. 056601, 2009.
- [19] D. Lee, J.-W. Kim, and B. G. Kim, "A new parameter to control heat transport in nanofluids: Surface charge state of the particle in suspension," *The Journal of Physical Chemistry B*, vol. 110, no. 9, pp. 4323–4328, 2006.
- [20] A. K. Nayak, R. K. Singh, and P. P. Kulkarni, "Measurement of volumetric thermal expansion coefficient of various nanofluids," *Technical Physics Letters*, vol. 36, no. 8, pp. 696–698, 2010.
- [21] E. K. Goharshadi, H. Azizi-Toupkanloo, and M. Karimi, "Electrical conductivity of water-based palladium nanofluids," *Microfluidics and Nanofluidics*, vol. 18, no. 4, pp. 667–672, 2015.
- [22] H. E. Ahmed, M. I. Ahmed, and M. Z. Yusoff, "Heat transfer enhancement in a triangular duct using compound nanofluids and turbulators," *Applied Thermal Engineering*, vol. 91, pp. 191–201, 2015.



Hindawi
Submit your manuscripts at
www.hindawi.com

