SIZE - AND SHAPE - CONTROLLED SYNTHESIS OF SILVER NANOSTRUCTURES FOR POTENTIAL HIGH THERMAL CONDUCTIVITY APPLICATIONS

by

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ABSTRACT

Nanofluids, which are based on the use of nanoscale particles suspended in a base fluid, have become a new alternative for improving heat management technology. Ultra fine and monodisperse solid silver particles are a very promising material for cooling fluids as they are known to exhibit the highest electrical and thermal conductivity of among metals. This project is focused on the effect of silver crystal size and shape on the thermal conductivity of the suspensions prepared at various concentrations in ethylene glycol, a typical cooling fluid. The crystal size and shape at the nanoscale are controlled by the synthesis conditions and the presence of shape-control agents like chloride salts. The specific shape-control on the silver nanostructures was achieved by the proper selection of the mole ratios of PVP/Ag in the starting solutions and the type and level of chloride salts such as NaCl and FeCl₂. which were significant for the final formation of the silver nanostructures (faceted crystals, wires, rods). These nano structures were remarkably monodisperse in size; the particle diameter could be controlled in the 30 - 50 nm range and the rod or wire thickness in the 24 -127 nm range. In the case of KCl and CaCl₂, the formation of silver nanowires (SNWs) exhibited a very uniform thickness that could be tuned within the range of 40 - 130 nm at 30 minutes of the reaction mixture. UV-Vis measurements evidenced the plasmon peak at ~387 nm and clear shoulders at ~357 nm that are indicative of the formation of elongated nanostructures. Synthesized nanostructures were characterized by X-ray diffraction (XRD) and UV-Vis spectroscopy, scanning electron microscope (SEM) and transmission electron microscope (TEM). The influence of size and shape properties, stable dispersion between nanorods and nanowires showed a slight enhancement of thermal conductivity when silver nanostructures (10-15% v/v) were suspended in the base fluid.

RESUMEN

Los nanofluidos se han convertido en una alternativa para mejorar la tecnología de gestión térmica que se basa en el uso de partículas a nanoescala suspendidas en el fluido base. Un material muy prometedor, basado en el uso de partículas ultra finas y monodispersas en los fluidos de enfriamiento, es la plata la cual presenta mayor conductividad eléctrica y térmica de entre los metales. En este proyecto, se centra en la evaluación del efecto del tamaño del cristal de plata y el control de la forma en la conductividad térmica de las suspensiones preparadas a diversas concentraciones en glicol de etileno, un típico fluido de enfriamiento. El control del tamaño de cristal y la forma a nanoescala se trató mediante la selección adecuada de las condiciones de síntesis y la presencia de agentes de control de forma utilizando sales de cloruro, tales como NaCl y FeCl₂ cual el uso de estas sales fueron significativas para la formación final de la plata dando nanoestructuras (cristales facetados, alambres, varillas). Estas nanoestructuras fueron monodisperas notable en tamaño y su dimensión pudo ser controlada en un intervalo de 30 – 50 nm (partículas) y 24 – 127 nm de espesor para las barras o alambres. En el caso de KCl y CaCl₂, la formación de nanoalambres de plata exhibió un espesor muy uniforme que podría ser sintonizado en el rango de 40 – 130 nm a los 30 minutos de la mezcla de reacción. UV-Vis evidencia el pico de plasmones en ~387 nm y ~357 nm del que son indicativos a la formación de nanoestructuras alargadas. Las nanoestructuras sintetizadas se caracterizaron por difracción de rayos X (DRX), espectrofotómetro de absorción de luz (UV-Vis), microscopio electrónico de barrido (SEM) y microscopio electrónico de transmisión (TEM). La influencia del tamaño y las propiedades de forma de las partículas, dispersión estable entre nanobarras y nanoalambres mostraron un leve aumento en las medidas de conductividad térmica cuando nanoestructuras de plata (10 - 15 % v/v) se suspendieron en el fluido base.

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Dedicated to ...

Gloria García

Modesto Marcano

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1 INTRODUCTION

Conventional heat transfer fluids lack suitable cooling efficiency due to their poor heat transfer properties. A direct consequence is the undesirable increase in the size of the overall heat management system [1]. In order to promote heat dissipation, the area available for exchanging heat within the heat transfer fluid may be increased. On this basis, novel applications of nanotechnology seek a new type of cooling fluid, so called *nanofluids*, consisting in the stable suspension of nanometer sized solid particles in conventional refrigerants.

Nanofluids can be prepared by two methods: (i) the direct evaporation method in which the nanoparticles are formed within the base fluids or (ii) the two-step method that involves the formation of nanoparticles and their subsequent dispersion in base fluids [2]. The disadvantage of the first route is that only low vapor pressure fluids are compatible with this option.

Silver nanoparticles have been widely studied because of their optical, thermal and electrical properties. The use of silver in nanofluids is more recent. Patel *et al.* observed increases in fluid thermal conductivity of up to 21% in their recent study on the behavior of Au and Ag nanoparticles dispersed in water and toluene. These results were achieved at extremely low nanoparticle loading (0.011 vol %) [1]. Moreover, experimental studies on thermal conductivity using the transient hot probe method for metal based-nanofluids

showed a 30 to 40 percent increase in the corresponding thermal conductivity for a 0.1 vol% concentration of Ag nanoparticles and 6.0 vol% concentration of Fe nanoparticles [3]. The present research addresses the systematic evaluation of nanofluids consisting of silver nanoparticles suspended in conventional cooling fluids. In particular, our work is focused on the evaluation of the effect of silver crystal size and shape on the thermal conductivity of the suspensions prepared at various concentrations in ethylene glycol, a typical cooling fluid. Silver nanostuctures will be produced in ethylene glycol at various polyvinyl pyrrolidone to silver ratios (PVP/Ag) in presence of NaCl and other inorganic salts. PVP and Cl⁻ ions are expected to affect the crystal and hence, the final particle shape [4]. The thermal conductivity of the Ag-based nanofluids, prepared at various volumetric loads, will be measured by the transient hot wire technique.

1.1 METAL BASED NANOFLUIDS: APPLICATION AND CHALLENGES

In applications for enhancing heat transfer, *nanofluids* may be capable of conducting heat on an order of magnitude higher than that predicted for similar suspensions by conventional theories. A strong temperature dependence of the thermal conductivity and a threefold higher critical heat flux than that of base fluids are also expected for this type of fluids. Nanofluids would represent several advantages over cooling fluids, for example, higher cooling rates, decreased pumping-power need, reduced inventory of heat transfer fluids, reduced friction coefficient and improved wear resistance. Also, nanofluids have also opened novel technological applications such as the development of new coolants and the miniaturization of heat exchangers [1]. One of the major challenges in the synthesis of metal nanocrystals has been controlling the population of the various types of shape and size. Regarding nanofluids for thermal conductivity applications, there is still a gap related to the actual effect of size and shape on the corresponding thermal conductivity. An additional challenge is keeping those nanoparticles stable in suspension. Surfactants are generally used to prevent particle agglomeration during nanoparticle formation and promote the formation of nanoparticles with different shapes.

Although the use of surfactants to stabilize silver nanoparticles in a solvent has been suggested, there is still a lack of detailed studies in this area. T. Cho, I. Baek, J. Lee and S. Park [5] used a polyol synthesis with silver nitrate as salt precursor and poly(acryl-amideco-acrylic acid) as dispersion stabilizer. Different concentrations of the silver nanofluid (1000 - ~10000 ppm) were prepared to measure thermal conductivity using the transient hot wire method. Although the study did not determine a control shape for the thermal conductivity measurement, the silver particle size became smaller and the degree of particle size distribution correspondingly increased according to the amount of dispersion stabilizer used. The average particle size was about 10 nm when the PAA-co-AA/AgNO₃ ratio was greater than 1. Thermal conductivity improved by 10, 16, and 18% as the concentration of silver particles in the nanofluid increased to 1000, 5000 and 10000 ppm. A better understanding of the mechanisms involved with this rise in thermal conductivity becomes fundamental to building a new series of high-efficiency devices for cooling systems to multiple-electronic devices.

1.2 MOTIVATION

Enhancing heat transfer for the operation and effective maintenance of devices has been the focus of many industrial sectors. With the unfavorable increases in heat loads which in some cases exceed 25 kW and heat fluxes caused by smaller, more powerful electronic and mechanical devices, improving cooling properties becomes indispensable to allowing those devices to work with improved performance.

A new alternative for improving heat transfer is based on the use of ultra fine and monodisperse solid particles in cooling fluids. A major problem with this approach, which uses millimeter or micrometer sized particles, is related to the rapid settling of the particles, erosion of piping systems and clogging and high pressure drop in the fluids bearing those particles. Furthermore, the size and concentration of the particles in contact with the fluid has a significant influence on the corresponding heat transfer capacity [6]. Nanoscale particles suspended in base fluid, also known as *nanofluids*, are expected to improve heat management technology while offering a great potential for further development of high performance, compact, cost-effective liquid cooling systems [7]. Compared to micronsized particles, nanoparticles are engineered to have larger relative surface areas, high mobility, better suspension stability than micron-sized particles, and a significant increase of the thermal conductivity. These features make nanofluids a promising working medium as coolants, lubricants, hydraulic fluids and metal cutting fluids [8-10].

Metallic silver is known to exhibit the highest electrical conductivity and thermal conductivity of among metals, making it a very promising material for electrical contacts

and an additive for conductive adhesives among other applications. Kang *et al.* [9] showed that the thermal performance of a heat pipe containing a silver-nanofluid is higher than that of a conventional heat pipe. Accordingly, the ability to the size/shape-controlled synthesis of Ag nanostructures provides a valuable opportunity to experimentally and systematically study the relationship between their functional and structural features and the corresponding thermal conductivity in the nanofluids.

On the above basis, the present work will seek to optimize a simple method to synthesize silver nanoparticles in polyol media. Synthesized nanoparticles will be then suspended in fresh ethylene glycol solution to obtain the corresponding nanofluid. This nanofluid will be then tested to determine its thermal conductivity as a function of silver particle shape and concentration.

1.3 OBJECTIVES

1.3.1 Main Objective

The main goal of the present research is to prepare silver-based nanofluids and determine the effect of nanoparticle size, shape and concentration on the corresponding thermal conductivity.

1.3.2 Specific Objectives

To achieve the main objective it was necessary to complete the following steps:

- Optimize a polyol-mediated synthesis approach to produce silver nanoparticles of different sizes and/or shapes
- (ii) Characterize as-synthesized nanoparticles on a structural, morphological and functional basis
- (iii) Determine suitable conditions to prepare stable suspensions of silver nanoparticles in ethylene glycol solutions
- (iv) Measure the specific thermal conductivity of the silver nanofluids as a function of silver size and shape and concentration.

1.4 THESIS CONTENTS

Chapter 1 gives an introduction to the thesis and hence provides the motivation and objectives for the project. Chapter 2, an overview of the literature, responds to the study of nanofluids by the initial step of process in silver synthesis nanostructures and thermal conductivity. Section 2.5 explains how chloride salts can affect the process of formation in the particle. Chapter 3 deals with the materials and synthesis procedures that were used to prepare and characterize silver nanofluids. Chapter 4 discusses the results obtained for investigations into Ag crystal structural, optical properties and morphology of the final product according to the chloride salts chosen. Thermal conductivity will also be discussed. A summary of all the results obtained and some recommendations are given in Chapter 5.

2 THEORETICAL BACKGROUND

2.1 NANOFLUIDS FEATURES AND CANDIDATE MATERIALS

Silver is a technologically attractive material due to its extremely high electrical conductivity in the bulk and its unusual optical properties that depend on size and shape at the nanoscale [9-16]. Intensive research efforts have been made to control the particle features to realize desirable and novel silver properties, which are distinctive from the bulk solids due to their small sizes. Furthermore, the development of new options to tune the shape of the nanoparticles is also of great interest since this capability would also contribute to the tailoring of the functional and thermal properties of the corresponding nanofluid. Hence, the thermal conductivities of fluids that contain suspended solid metallic particles, especially silver, could be expected to be significantly higher than those of conventional heat transfer fluids as is observed in the Table 1.

	Material	Thermal Conductivity (W/m*K) ^a
Metallic Solids	Silver	429
	Cooper	401
	Aluminum	237
Nonmetallic solids	Diamond	3300
	Carbon nanotubes	3000
	Silicon	148
	Alumina (Al2O3)	40
Metallic liquids	Sodium at 644 K	72.3
Nonmetallic liquids	Water	0.613
	Ethylene glycol	0.253
	Engine oil	0.145
^a At 300 K unless otherw	rise noted	

Table 1. Thermal Conductivity of Different Materials [7]

2.2 SIZE- AND SHAPE-CONTROLLED SYNTHESIS OF SILVER NANOSTRUCTURES

A wide variety of size- and shape-controlled syntheses have been developed to produce spherical nanoparticles, nanorods, nanowires, and nanocubes of silver. [13, 16]. Condensation methods allow a better control with morphology and size of the particle. In this approach, silver nanoparticles are chemically produced by reduction of silver compounds or complexes in aqueous or organic media. Some known reducing agents are sodium citrate, hydrogen, hydrogen peroxide, hydroxylamine, hydrazine, formaldehyde and its derivatives, ascorbic acid [12-14]. Although both inorganic and organic reducing agents are used for producing silver particles from solution, organic reducing agents present the advantage of forming finer particles [17-18].

Another option to produce silver nanoparticles is the so-called *polyol process* that has attracted more attention due to its simplicity; the polyol acts as both solvent and reducing agent. This alternative is a useful method for producing highly pure, fine, and monodisperse particles of uniform shape. The factors that influence the growth kinetics in this solution-phase synthesis include: the concentration of metal precursor, the rate of reduction, the presence of a capping agent and the specific adsorption of a capping agent to a particular crystallographic plane. In this regard, a drastic change in particle shape was observed when the synthesis took place in presence of polyvinylpyrrolidone (PVP) that also acted as a crystal habit modifier [12, 19]. Although polyol itself is not effective enough as a protective agent for preventing the particle-particle adhesion and their subsequent sintering [20-21], the addition of a protective agent is essential for preventing aggregation and coalescence of the silver primary particles during the growth step. PVP exhibits the

best protecting properties and is therefore selected in this project. The main outcomes of another related works can be summarized as follows:

Xia *et al.* [22] produced silver nanocubes in large quantities. The morphology and size of the product were found to strongly depend on reaction conditions such as temperature, the concentration of AgNO₃, and the molar ratio between the repeating unit of PVP and AgNO₃. C-X Kan *et al.* [23] obtained uniform sizes of silver nanorods and nanowires when the ratio of PVP/AgNO₃ varied in the 3 - 8 range, in which (1 1 1) planes of Ag crystal and the highly selective polyvinylpyrollidone adsorption on the (1 0 0) planes of Ag crystal nuclei were favorable for the formation of Ag nanorods and nanowires. B. Wiley *et al.* [24] explored some common ionic species in the shape-controlled synthesis; minor amounts of NaCl and other inorganic salts were added during the standard polyol synthesis. They showed that inorganic ions have a favorable influence on the nucleation process of crystals than organic ions contained in the surfactants or polymers, because of the relatively small sizes associated with nuclei. J. Jiu *et al.* [25] suggest that the Cl⁻ ions improve the formation of twinned crystals. They also noticed that the molar ratio of PVP to AgNO₃ affected the yield and morphology of nanorods.

T. Maiyalagan [26] found the catalytic properties of Ag nanorods originated from its affinity to chloride ions; the possibility of an extraordinary electrocatalytic effect of the synthesized Ag was associated with the morphology of the nanorods. B. Wiley, T. Herricks, Y. Sun and Y. Xia [24], used inorganic species in a polyol synthesis using an Ag/PVP molar ratio of 1.5 for a concentration of 94 mM of silver nitrate and 22 mM NaCl. The final product was monodisperse single crystals in the 20 – 80 nm size range. C-X Kan

et al [23] reported that morphology and size of the Ag particles are significantly dependent on the experimental parameters such as the PVP/AgNO₃ ratio and temperature. They produced nanorods, polyhedral and truncated cubes. However, the twinned structures do not exist separately, but in coexistence or even competition with a single crystal, depending on the experimental conditions.

2.3 THE POLYOL PROCESS

2.3.1 Introduction

Polyol, or monoalcohols, are used as reducing agent to reduce zero-valence state ions of the noble metals and more electropositive metals such as copper, gold, silver, nickel, etc [24, 27]. Metal reduction in alcohols has become in a suitable route to provide non agglomerated particles and controlled morphology. The use of liquid polyol has multiple properties which has attracted attention due to simplicity of kinetically controlling conditions in a homogenous solution. Fievet introduced originally the polyol method as an alternative to reduce size particles to micrometer and submicrometer scale to monodisperse metallic particles [27]. The polyol process acts as solvent, reducing agent and crystal growth medium for the silver particles into the heated solution, and in some cases as a complexing agent for the metallic cations.

2.3.2 Reduction in Liquid Polyols

The reduction of metallic compounds in liquid polyol allows the formation of metal powders on a micrometric or nanometric scale. For easily reducible metals such as silver, the reaction can be carried out at low temperatures from a suitable precursor. In this case a soluble salt starting compound such as silver nitrate was used in the polyol; in contrast other metallic salts use high temperature up to the boiling point at the polyol around 200 °C. The main product of ethylene glycol (EG) (CH₂OH-CH₂OH) was diacetyl (CH₃COCOCH₃), metal ions are reduced by acetaldehyde, and an intermediate generated by degrees through dehydration of EG. The dehydration reaction of ethylene glycol must be reversible since the rate is affected by the succeeding reaction of acetaldehyde with metal ions and the reduction rate of metal ions strongly depends on the metal-ion species in the polyol process [28]. Therefore, since water and monoalcohols have high value of relative permittivity, they are able to dissolve to some extent of ionic inorganic compound [27-29]. Table 2 shows comparison values for anhydrous ethylene glycol and water properties as solvents for reducible noble metals.

Liquid Base	Molecular Weight (g/mol)	Molecular Formula	Molecular Structure	Boiling point at 1 atm (°C)	Density (g/cm ³⁾	Relative permittivity
Water	18.02	H_2O	• о н н	100	1.000	78.5
Ethylene Glycol	62.07	$C_2H_6O_2$	H H OH – C – C - OH H H	194.8	1.115	40

Table 2. Ethylene Glycol and Water properties [29]

2.3.3 Nucleation and Growth Mechanism of Silver Nanostructures

The average diameter and size distribution of particles is dependent on the reaction temperature and the precursor/polyol ratio. In this case, the formation of metal particles involved the following steps: reduction of metal ions to metal atoms, aggregation of metal atoms to form metal nuclei, growth of nuclei to metal nanoparticles and finally stabilization of metal nanoparticles by stabilizers, in this case PVP. Figure 1 shows a diagram of the formation of process of metal nanoparticles from metal ion. The molecular ratio between the repeating unit of PVP and AgNO₃ plays a crucial role in determining the geometric shape of the product. Thus, PVP plays an important role as a coordination reagent and architecture soft-template through O-Ag bonding. In order to obtain particles with such well-defined morphological characteristics a general condition must be fulfilled: nucleation and growth must be two completely separated steps.



Figure 1. Formation process of metal nanoparticles in homogeneous solution [27].

The process of nucleation and growth of the reaction mixture of silver particles has been established in order to control the size and shape control at nanoscale. In our case, as silver do not show intermediate solid phase, the reaction involves the reduction of the oxidized silver species by ethylene glycol, nucleation and growth of the metallic silver. Ag⁺ ions are reduced to Ag⁰ (where nucleation occurs). In this step, a thermal energy for the nuclei formation exists, allowing a defect to form or be removed depending on its energetic favorability as shown in Figure 2. Growth of the nuclei is due to the aggregation of single crystallites that tend to grow from the dissolution of small particles; this is called the *Ostwald ripening process* [27]. Then in absence of Cl⁻ ions, the initial seeds start to grow into irregular particles [16].



Figure 2. Formation of silver particles through nucleation and growth mechanisms [28].

Figure 3 represents LaMer's diagram which describes the understanding process of non agglomerated nanoparticles. In the solution, a spontaneous nucleation takes place rapidly where nuclei are formed in a short period time. The concentration of the metal is reduced until it reaches a critical level called *supersaturation*. If the metallic silver is generated slowly and the nucleation rate is sufficiently high, then nucleation level suddenly lowers the concentration below to a critical nucleation level [20, 27]. The nuclei start to grow by deposition of metallic silver until the system reaches equilibrium where no more nuclei appear to start the growth stage. The formed primary particles results in polydisperse secondary particles of different shapes without a protective agent in order to define morphological characteristics of the particles during their growth stage. The polyol process

itself is not effective enough as a protective agent to prevent the small noble metals particles from coalescing.



Figure 3. LaMer's diagram to the production of monodisperse systems [29]

In order to obtain a monodisperse system, the growth step must be controlled by adding a polymeric protective agent that adsorbs onto the metallic particles, ensuring their steric stabilization while they are growing. Polyvinylpyrrolidone (PVP) has been selected in this case and its chemical structure is shown in the Figure 4.



Figure 4. Structure of the polyvinylpyrrolidone (PVP)

The nanoparticle surfaces are attracted to the organic links with electron donor atoms such as oxygen or nitrogen. These atoms are capable of providing strong bonds, making possible the formation of well shaped nanoparticles [27-29].

The addition of Cl⁻ anions to the polyol solution has been a important factor to produce well-defined silver nanostructures. It is found that oxygen must be removed from the syntheses in the presence of Cl⁻ anions in order to obtain a shape control of the particle. In contrast, the use of only PVP causes the growth of irregular particles. After Ag seeds form an enhanced nuclei size, changes in the structure can be tuned in the early growth stage. These structures, which include single crystal, single twinned or multiple twin morphology, may be seen in Figure 5 [28, 29]. In this case, we used NaCl, FeCl₂, KCl, BaCl₂, and CaCl₂ which have been shown to influence the morphology of the final product.



Figure 5. Mechanism and growth of the nanostructures Ag [4].

The use of chloride as a reagent in the synthesis can cause an enhanced oxidation and promote an etching in the twinned particles, allowing seed single crystal to grow into particles. It is found that the edges and corners of the silver nano seeds become tuned and sharp due to high crystallization [30-31]. Thus, Cl⁻ anions provide a convenient way to prevent rapid aggregation of the particles as electrostatic stabilization between particle-particle and facilitate their growth into nanostructures. X. Tang *et al* [30] indicated that the proposed mechanism of oxidative etching and growth for the case of multiple twinned particles can be possible through defects among single-crystal tetrahedron subunits of decahedral particles. These particles provide high-energy sites for atomic addition, leading to 1D silver particles via anisotropic growth along the <110> direction. Meanwhile, pentagonal SNW's showed a selective deposition of Ag atoms on the wedges. Specifically, the (111) end facets of the decahedral seeds are reconstructed, conserving the diameter, while new (100) edge facets are formed and continually elongated [31] as is

shown in Figure 6. In addition, O_2 can be adsorbed and dissociate on silver surfaces and block the (111) reactive sites from adding Ag atoms in a convenient way [18, 19].



Figure 6. Cubic, triangular bipyramidal, rods and wires of Ag nanocrystals bound by only (100) and (111) faces [30].

Minimum amounts of chloride anions introduced in the synthesis play an important role in the polyol synthesis of SNW's. An understanding of the chloride ion properties reveals that it provides electrostatic stabilization for the initially formed silver seeds. Also, chloride ions can reduce the concentration of free Ag^+ ions in the solution through the formation of AgCl nanocrystallites. The formation of AgCl would allow a slow release of Ag^+ ions which facilitates the high yield formation of the thermodynamically more stable multiple twinned particles required for wire growth [30]. According to X. Tang *et al* [30], these formed AgCl particles can serve as seeds of Ag anisotropic nanoparticles. In the formation process of the particle, etching rate will increase if the concentration of Cl⁻ ions also increases. Therefore, the oxidative etching rate becomes higher and small silver particles can be etched in the presence of O₂ [24-25]. Following growth rates of silver seeds also increase the crystal growth and competitively oxidative etching occurs. For that reason, the relative rate of crystal growth and oxidative etching strongly depends on shapes of Ag particles [30]. The literature explains that the shapes of the final products depend not only on the stability of crystal structures against etching by CI^{-}/O_{2} but also the density of Ag^{0} atoms around the growing nuclei [30]. X. Tang *et al.* [30] also explained that a high related ion concentration around the nuclei can create an environment with high twinning probability for the formation of MTPs from which pentagonal 1D rods and wire are grown. In addition, five-twinned 1D products are favorable at higher concentrations of Ag^{+} ions, whereas single crystal cubes are preferentially formed at lower concentrations of Ag^{+} ions.

The literature also shows that both the cation and anion are necessary for the successful production of different shapes of Ag such as e.g. nanowires. But also reflects that although shapes product particles are independent of cation species, there are significant differences in the yields and sizes of the Ag products when using different chloride salts. M. Tsuji *et al* [32] based on the observations; it seems that cation ions probably influence Ag product distributions under present experimental conditions.

2.4 MATERIALS CHARACTERIZATION TECHNIQUES

2.4.1 X-Ray Diffraction (XRD)

X-ray diffraction technique is the most well known way to identify crystalline phases and structural properties such as preferred orientation, grain size and defect of structure and phase composition. The crystal structure analysis of silver nanostructures were carried out using the Cu-K α radiation and β Ni filter in a Siemens D500 powder x-ray diffractometer (Figure 8). XRD patterns were recorded in the 2 degrees range of 30° - 80° with a 0.02° step and a sampling time of 2 seconds. Diffraction events are a consequence of a beam of

high electrons colliding with a metal target. The atoms present in the target go to the excited states and decay back to their original ground state, emitting X - rays. The diffraction patterns are formed by interference of diffracted beams (Figure 7).



Figure 7. Basic Principles of diffraction phenomenon

The X- ray radiation is scattered by atoms regularly arranged in a lattice possessing interatomic distances of a magnitude comparable to the wavelength of the incident radiation. Crystal structure is related to the constructive interference of the optical light difference between the incident and scattered beam which is a segment ABC and must be an integer number (n) of x radiation wavelength which is considered by Bragg's Law. The equation is:

$$n \lambda = 2d \sin \theta \qquad \qquad \text{Eq. 1}$$

where (n) is the number of integer wavelength of difference in optical path, (λ) is the wavelength of the used radiation, (θ) is the diffraction angle and (d) is an interplanar distance [33-34]. The information recollected of the diffracted electrons is used to determine crystallographic information of the Ag samples analyzed. The average crystallite

size is determined by Scherrer's equation where B corresponds to the full width at half maximum of the broad diffraction line on 2 theta degree measured in radians as in the following equation:

$$t = \frac{0.9\lambda}{B\cos\theta}$$
 Eq. 2

To determine lattice parameter of the silver nanostructures the following equation was also used:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$
 Eq. 3

Where d is the interplanar distance, h,k,l are miller indexes and a is the lattice parameter.



Figure 8. X- Ray Diffractometer Siemens D500- Engineering Science and Materials Department at UPR – Mayaguez Campus.
2.4.2 Ultraviolet – Visible Spectroscopy (UV-Vis)

Ultraviolet light is the electromagnetic radiation of a wavelength shorter than that of visible light. The electronic excitation occurs when ultraviolet and visible region are absorbed from the sample. This excited species returns to its original state through a process called relaxation; emitted energy can be transformed into light [29]. Different materials may absorb light differently to show different colors according to the size and shape of the particles.

When a beam of monochromatic UV light with intensity I_0 , passes through a solution, the optical transmittance *T* is defined by;

$$T = \frac{I}{I_0}$$
 Eq. 4

where I and I_0 are the ultraviolet light intensities before and after passing through the sample cell. This sample cell of UV must have zero or 100% absorption for a given monochromatic ultraviolet light or a range of wavelengths [35-37]. The percent of transmittance is:

$$\%$$
T = T*100 Eq. 5

The absorbance (A) is defined by,

$$A = \log\left(\frac{1}{T}\right)$$
 Eq. 6

The absorbance of photons of light *A* is described through the Beer-Lambert law, which is considered for a monochromatic radiation. Although Beer's law is valid only at low concentrations, another way of expressing it is;

$$A = \varepsilon^* l^* c \qquad \qquad \text{Eq. 7}$$

Where absorbance (A) is proportional to the path length (l) and the analyte concentration (c) and (ε) is measured by the amount of light absorbed per unit of concentration.



Figure 9. Schematic of a wavelength single beam UV-Vis absorbed radiation

Some various metals such as Ag, Au, etc. can exhibit a plasmon by its optical properties. The study of the plasmon consists in a quantum of plasma oscillation in a metal that is a collective longitudinal excitation of the conductor electron gas [37-39]. Metal nanostructures convert light into localized electric fields (E fields) or as waveguide to route light to desired locations with nano scale precision. The incident light and free electrons have a strong interaction due to the size and shape of the nanostructures in which light could be manipulated. These key components are due to the support of the surface plasmon polarization modes. Rycenga *et al* [35] agree that metallic nanostructures can be differentiated based on the plasmonic modes which support: localized surface plasmons (LSP) or propagating surface plasmons (PSP). In LSP, the time varying electric field associated with the light (E_o) exerts a force on the gas of negatively charged electrons in the conduction band of the metal and drives them to oscillate collectively. At a certain

excitation frequency (w), this oscillation will be in resonance with the incident light, resulting in a strong oscillation of the surface electrons, commonly known as a localized surface plasmon resonance (LSPR) mode. This phenomenon is illustrated in Figure 10A. Structures that support LSPRs experience a uniform E_o when excited by light since their dimensions are much smaller than the wavelength of the light. In contrast, PSPs are supported by structures that have at least one dimension that approaches the excitation wavelength, as Figure 10B shows. In this case, the *Eo* is not uniform across the structure and other effects must be considered [35, 37].



Figure 10. Scheme of two types of plasmonics metallic nanostructures, (A) the nanostructure, wavelength of light and the free electrons can be displaced from the lattice of positive ions and collectively oscillate in resonance with the light, (B) the nanowire has one dimension much larger than the wavelength of light. [35].

The excitation of outer electrons is involved in the absorption of ultraviolet radiation. In this process when an atom absorbs energy, electrons are stimulated from their ground state to an excited state. The vibrations accompanied with rotations of the atoms or molecules have discrete energy levels, which are considered being on top of each electronic level [39]. Where this occurs, the absorbing species containing p, s, and n electrons promote shifts in

the wavelength. For *n* to pi^* transitions which involve an electron from a nonbonding electron pair to an antibonding pi^* orbital, a shift to higher energy and shorter wavelengths is observed as a blue shift. The excited state emerges and the solvent molecules do not have time to rearrange in order to stabilize the excited states, giving as a result an increase in the energy of the transition.

The transitions involving a moving electron from a nonbonding electron pair to an antibonding pi^* orbital are known as pi to pi^* transitions. A shift to lower energy and longer wavelengths is considered as a red shift. This could be due to an increase of the ground state energy or lowering of the excited state energy and its energy of transition [38, 39].



Figure 11. Beckman Coulter DU 800 UV/Visible Spectrophotometer, NANOmaterials Processing Lab-Engineering Sci. and Materials Department, University of Puerto Rico, Mayaguez campus.

2.4.3 Scanning Electron Microscopy (SEM)

SEM analysis was used to determine morphology of the silver particles. The use of an electron beam for imaging purposes is possible through vacuum conditions which avoid collisions between electrons and air molecules. This convenient conditions will allow that accelerated electrons and kinetic energy be dissipated as an array of signals produced by electron-sample interactions when incident electrons are decelerated, samples are required to have an electrically conductive surface. These signals include; secondary electrons, back- scattered electrons, photons and diffracted electrons, visible light and heat. The SEM images are produced through secondary electrons and a special detector that can be used to build a surface image. The sample's surface is scanned point by point to create the image of the investigated portion of sample surface [29, 36]. The JEOL model JSM-7500F Scanning Electron Microscope was used in the present work.



Figure 12. Scheme of Scanning Electron Microscope



Figure 13. JEOL model JSM-7500F Scanning Electron Microscope, IFN Nanoscopy facility, Dept. of Physics, University of Puerto Rico, Rio Piedras Campus

2.4.4 Transmission Electron Microscopy (TEM)

TEM analyses were used to determine morphology of the synthesized Ag particles, size and distribution of the samples. A beam of electrons is generated through at the top of the lenses in the column microscope, since electrons are not able to move in the atmosphere, a column chamber of the TEM maintains a high vacuum above 10⁻⁵ Pa to enhance mean free path of electrons. This beam traveling direction with negative charge can be altered with electromagnetic lenses that correspond to condenser, objective and projective lenses [29, 34, 36]. The electron beam is parallel to the specimen by using the condenser lens which strikes the specimen to determine its crystal information such as composition, structure, etc. Interactions between the beam and sample produce different kind of signals. In our case,

secondary and back scattered electrons provide information about the surface composition and the internal structures such as energy dispersive X ray spectra and EELS [29].



Figure 14. Scheme of Transmission Electron Microscope



Figure 15. Transmission Electron Microscope (TEM) Carl Zeiss LEO 922 EFTEM and JEOL JEM-2200FS high resolution TEM (HRTEM), IFN Nanoscopy facility, Dept. of Physics, University of Puerto Rico at Rio Piedras

2.5 FUNDAMENTALS OF THERMAL CONDUCTIVITY

Thermal conductivity is the study of the capability of a medium to conduct heat. Hence it is necessary to introduce Fourier's law which agrees that the heat flux in the direction of heat flow is proportional to the temperature gradient in that direction. For one dimensional problem, this expression can be written as,

$$q_x = \frac{Q_x}{A} = -k \frac{dT}{dx}$$
 Eq. 8

The rate in which heat energy is transferred from one point to another point in a homogenous material is proportional to temperature gradient inside material [40-47]. In base of the above equation q_x is the heat flux in the *x* direction, Q_x is the heat flowing in the *x* direction, *A* is the area perpendicular to *x* through which it flows, and *k* is the constant of proportionality, known as the *thermal conductivity* '*k*' can be used to characterize the materials; the larger the '*k*' value the more conductive the material will be [1, 29, 44, 47]. The unit of thermal conductivity is W/m·K. Since the thermal conductivity is a measure of the capability of a medium to conduct heat, it is always positive. The possibility of a theory to predict thermal conductivity of nanofluids has been converted into an unsolved problem although some models exist to calculate the apparent conductivity of the binary mixture [42, 45].

2.5.1 Models of Thermal Conductivity in Fluids

For solid-liquid suspensions, semi empirical correlations exist to analyze an effective way to calculate the apparent conductivity in two phases mixtures. Currently, there is no theory to predict exactly thermal conductivity in nanofluids. Through the use of the Maxwell model for thermal conductivity, an approach has been observed to the theory of low concentrations, micron size particles which is counterproductive in high concentrations [42]. This model is expressed in the equation below,

$$k_{eff} = \frac{k_p \phi_p (dT/dx)_p + k_b \phi_b (dT/dx)_b}{\phi_p (dT/dx)_p + \phi_b (dT/dx)_b}$$
Eq. 9

where k_p is the thermal conductivity of the particle, k_b is the thermal conductivity of the base fluid and φ' is the particle volume fraction of the suspension [43]. Maxwell's formula shows that effective thermal conductivity of nanofluids relies on the thermal conductivity of the spherical particle, the base fluid and the volume fraction of the metallic particles. There are parameters that affect thermal conductivity of nanofluids including volume fraction, base fluid, surface area, temperature, size and shape of the particle [1, 41-44].

However, Hamilton and Crosser proposed a developed model depending of the shape of the particle in the suspended fluid as function of the conductivities of the pure materials and composition [44]. This models represents that non-spherical shapes will increase thermal conductivity above that of spherical particles in the following equation,

$$k_{eff} = \frac{k_{p} + (n-1)k_{b} - (n-1)(k_{b} - k_{p})\emptyset}{k_{p} + (n-1)k_{b} + (k_{b} - k_{p})\emptyset} k_{b}$$
 Eq. 10

They introduced a shape factor, n, to account for the effect of the shape of the particles [42, 44], where n is the empirical factor given by $n=3/\psi$, and ψ is the particle sphericity, defined as the ratio of the surface area of a sphere with volume equal to that of the particle, to the

surface area of the particle. A comparison between Maxwell's model is a special case of the Hamilton and Crosser's model for $\psi = 1[44]$.

2.5.2 Effects of Colloidal Stability in Nanofluids

In order to promote the stability in the suspension of the nanofluids the addition of surfactants is necessary, even though surfactants might cause several problems in thermal conductivity measuring such as produce foam in heating and cooling in heat exchange systems and enlarge the thermal resistance between nanoparticles and base fluid, which may limit the enhancement of the effective thermal conductivity, it is still a convenient way to avoid agglomeration of nanoparticles resulting in the settlement and clogging [44].

The stability of a particle in solution is determined by the Van der Waals attractive forces and electrical double layer forces that exist between particles as they approach each other due to the Brownian motion [29, 42, 47]. If the attractive force is larger than the repulsive force, the two particles will collide, and the suspension is not stable. If the particles have a sufficient high repulsion, the suspensions will exist in stable state. For stable nanofluids or colloids, the repulsive forces between particles must be dominant.

The fundamental mechanisms that affect colloidal stability are divided into two kinds, one is steric repulsion, and another is electrostatic (charge) repulsion, as represented in Figure 16. For steric stabilization, polymers are involved into the suspension system, and they will adsorb onto the particles since silver nanofluids are very stable due to the protective role of PVP, as it retards the growth and agglomeration of nanoparticles by steric effect. For an electrostatic stabilization surface charge will be developed by preferential adsorption of ions. For that reason nanofluids are considered to be stable when the concentration or particle size of supernatant particles keeps constant.



Figure 16. Two methods of surfactants to prevent agglomeration (a) steric and (b) electrostatic stabilization.

2.5.3 The Effect of Brownian Motion

The indicative of the Brownian motion is the random movement of particles suspended in this case, in a liquid and the motion is due to collisions with base fluid molecules, which makes the particles undergo random walk motion [11, 42]. Thus, the Brownian motion intensifies with an increase in temperature as per the kinetic theory of particles [10]. The effectiveness of the Brownian motion decrease with an increase in the bulk viscosity.

2.5.4 Effects of Nanoscale Particles Clustering

The general effect of the clustering in the particles is that may exert a negative effect on heat transfer enhancement particularly at low volume fraction, by settling small particles out of the liquid and creating large regions of "particle free" liquid with high thermal resistance [1, 11, 42, 44, 47].

2.5.5 Interfacial Layer in the Nanoparticle Surface

Literature has shown that liquid-particle interface effect could enhance thermal conductivity in the layering of the liquid at the solid interface, by which the atomic structure of the liquid layer is more ordered than that of bulk liquid. Crystalline solids display much better thermal transport than liquids; such liquid layering at the interface would be expected to lead to a higher thermal conductivity [42]. Although the presence of an interface layer may play a role in heat transport, it is not to be only responsible for the enhancement of thermal conductivity [42-44].

2.5.6 Effect of the Size and Shape in Nanofluids

One of the parameters that can affect thermal conductivity measurement is the size of the particle. Teja *et al.* [41] considered its experiments using hot wire technique nanofluids containing silver nanoparticles of different sizes (20, 30-50, 80 nm) and volume fractions (1% and 2% v/v) with an estimated error of \pm 2%. The results provided that there was a decreasing in the thermal conductivity of silver nanofluids with decreasing particle size.

2.5.7 Thermal Conductivity Measurements by the Transient Hot Wire Technique

The importance of thermal conductivity is to demonstrate the enhancement potential of heat transfer in nanofluids. So far, thermal conductivity has been influenced by size and shape of the particle, base fluid and the volume fraction. In our case, we will use transient hot wire technique.



Figure 17. Thermal Conductivity, transient hot wire method, Center for Advanced Nuclear Energy Systems (CANES) in the Dept. of Nuclear Science and Engineering in Massachusetts Institute of Technology (MIT).

The transient hot wire method consists in applying a certain current to a thin platinum wire immersed in a base fluid, in this case ethylene glycol. The wire temperature increases because of its resistance. Since the diameter is negligible with respect to the wire length, the temperature in the wire will be very close to the temperature in the fluid. The increase in temperature in the fluid will be controlled by a thermal conductive process [48]. The temperature of the wire is determined by the corresponding resistance. A voltage is applied to the wire ends and the temperature is determined from a calibration curve. The calibration curve will determine the platinum wire resistance as function of temperature. To measure the resistance, a Wheatstone bridge circuit is used to reduce impedance error [35-38]. The transient hot wire is known by its fast and convenient technique to measure thermal conductivity.

3 METHODOLOGY

3.1 MATERIALS

All chemicals were reagent grade. Silver nitrate (ACS, 99.9+ %, Alfa Aesar) was used as metal precursor. The reducing agent and solvent used for silver particle synthesis was anhydrous ethylene glycol, EG, (99.8+ %, Sigma Aldrich). Polyvinylpyrrolidone (PVP Mw = 58,000, Sigma Aldrich) was used to prevent particles from aggregation as well as a shape modifier. Minor amounts of NaCl (99.9+ %, Acros Organics), FeCl₂ (99.7% purity, Alfa Aesar), KCl (99.9% purity, Alfa Aesar), BaCl₂ (99.8+ %, Alfa Aesar) and CaCl₂ (99.9% purity, anhydrous, Sigma) were also added to the PVP solution. These chloride salts were selected based on their capability as habit-controlling agents.

3.2 EXPERIMENTAL

The following schemes represent the experimental set up and the synthetic procedure followed to generate silver nanoparticles with controlled size and shape.



Figure 18. Synthesis set-up for silver nanoparticles via a polymer-mediated polyol process.

3.2.1 Materials Synthesis



Figure 19. Synthesis procedure for silver nanostructures via a PVP-mediated polyol process.

A modified version of the synthesis protocol developed by Wiley *et. al.* [24] was followed. In our case, different types and concentration of the chloride salts were used. Ethylene glycol (99.8% purity, anhydrous) was used as a reducing agent and solvent. AgNO₃ (ACS, 99.9+ %, Alfa Aesar) was the metal precursor and poly-vinyl pyrrolidone (PVP, MW 58,000 g/mol, 99.8%, Sigma Aldrich) was the capping agent to prevent aggregation of assynthesized particles. The PVP/Ag mole ratio was varied in the 0.5 - 3 range. Ethylene glycol solutions of AgNO₃ and PVP were simultaneously added to ethylene glycol previously heated up to 160°C. Minor amounts of NaCl (99+ % purity, Acros Organics), KCl (99.9% purity, Alfa Aesar), FeCl₂ (99.7% purity, Alfa Aesar), BaCl₂ and CaCl₂ (99.9% purity, anhydrous, Sigma) were also added to the PVP solution. The reaction mixture was kept to 160 °C, under a continuous heating condition provided by an oil bath, until all the AgNO₃ was completely reduced. Samples were withdrawn at various times during the onehour reaction stage. Silver nanostructures were recovered from ethylene glycol by centrifugation, washed with ethanol and stored in the same solvent. Figure 19 shows the corresponding experimental procedure.

3.2.2 Materials Characterization

SIEMENS D500 diffractometer with a Cu-K_{α} radiation was used to study structural analyses of silver products. The optical absorption spectra were obtained using a DU 800 UV-Vis Spectrophotometer. The samples were examined using a JEOL JSM-7500F scanning electron microscope (SEM) with an x-ray energy dispersive spectrometer (XEDS) to determine their elemental composition. The samples were also investigated using transmission Electron Microscope (TEM) a Carl Zeiss LEO 922 EFTEM and a JEOL JEM-2200FS high resolution TEM (HRTEM).

3.2.3 Preparation of Silver-Based Nanofluids

Ag nanostructures (wires and rods) synthesized by the above described method were dispersed in ethylene glycol and sonicated for one hour. Two types of nanofluids, each one of 75mL, were prepared. Silver wires synthesized after 30 minutes of reaction at NaCl/Ag and KCl/Ag mole ratios of 0.012 and 0.003 were used. The silver volumetric loadings were 5, 10, and 15% v/v. Additional details of the dispersion of silver nanostructures in ethylene glycol are shown in Figure 20.



Figure 20. Preparation of silver-bearing ethylene-glycol nanofluids.

3.2.4 Nanofluid Thermal Conductivity Measurements

Thermal conductivity measurements by the hot-wire technique were realized in collaboration with Dr. Tom McKrell of the Center for Advanced Nuclear Energy Systems (CANES), Department of Nuclear Science and Engineering at Massachusetts Institute of Technology (MIT). The hot-wire device used to measure the thermal conductivity of our nanofluids, consisted of a platinum wire coated with a polyester enamel that is immersed in the test fluid. The apparatus consists in Teflon coated platinum wire that is used as heater and thermometer through of the sample. The temperature and time on the platinum wire is measured while a current is applied through the wire. The accuracy in the measurements of the thermal conductivity coefficients due to the wire resistance was measured using an unbalanced Wheatstone bridge to reduce the impedance error. A Wheatstone bridge contains three known and one unknown resistance, (the platinum wire). This system also required a voltage source and voltmeters, (data acquisition board). The nanofluid is fed into inner cylinder to decrease the influence of the external environment. Then, the cell containing the nanofluid is placed into a high-accuracy cooling system and stabilized for

the reading of the data [28]. The fundamentals and details of the hot-wire technique have been described in previous sections.

4 RESULTS AND DISCUSSION

4.1 SYNTHESIS OF SILVER NANOSTRUCTURES

Silver nanoparticles were synthesized by reduction of silver ions in ethylene glycol media containing surfactant (PVP) and chloride species. The use of inorganic salts such as NaCl, BaCl₂, KCl, FeCl₂ and CaCl₂ were expected to induce the formation of crystals with different habits and shapes.

4.2 EFFECT OF THE PVP/Ag MOLE RATIO

4.2.1 Structural Characterization by X-Ray Diffraction (XRD)

Figure 21 shows typical XRD patterns for the solids synthesized at different molar ratios of PVP/Ag (0/1, 0.5/1, 1/1, 1.7/1, 2/1 and 3/1) and 30 minutes of reaction. The solids formed at earlier times consisted of partially reduced Ag agglomerated particles. The 30-minute reacted samples consisted of Ag-FCC; the average lattice parameter was estimated at 4.094Å, which is very close to the reported data for bulk silver (4.0862 Å) [22]. The average crystallite size for each PVP/Ag molar ratio, estimated by the Scherrer's equation, is summarized in Table 3. The data in this table evidences that a minimum increase in PVP concentration lead to a decrease in the crystallite size in the range of 1-2 of PVP/Ag molar ratio with 40 nm, respectively.

Larger particles were showed in molar ratios of 0/1, 0.5/1 and 3/1 with an average crystallite size of ~57 nm. When PVP is introduced, it is believed that selective adsorption of PVP molecules onto silver planes could greatly reduce the growth rate. Y. Sun *et al.* [22] explained that the selective interaction between PVP and various crystallographic planes of FCC silver could greatly reduce the growth rate along the (100) direction and/or enhance the growth rate along the (111) direction [16, 31].



Figure 21. XRD patterns of Ag powders synthesized at 30 minutes of reaction and different PVP/Ag mole ratios in the 0 - 3 range. All main peaks correspond to the FCC-Ag phase.

PVP/Ag Molar Ratio	Average Crystallite Size (nm)	Standard Deviation
0	66	5.3
0.5	55	17
1	44	6.1
1.7	40	2.3
2	46	3.4
3	51	16

 Table 3. Average crystallite size of silver samples synthesized at various PVP/Ag mole ratio. The AgNO3 starting concentration was 94 mM.

4.2.2 UV-Vis Measurements

Figure 22 and 23 show the absorption spectra of silver nanoparticles suspended in ethanol. The samples were synthesized from a 94 mM AgNO₃ solution in ethylene glycol using PVP/Ag molar ratios of 1 and 1.7, respectively, and 10 minutes of reaction. Both spectra exhibited the typical plasmon peak centered on 440 nm and 422 nm, respectively, which may suggest a slight decrease in size at higher PVP/Ag mole ratios. Figure 24, shows the absorption spectrum for the silver samples synthesized at different reaction times and a PVP/Ag mole ratio of 3. The broad peak centered on approximately 450 nm can be attributed to the surface plasmon resonance band of silver nanoparticles with low aspect ratio and large polydispersity [25]. A minor but evident shoulder at ~350 nm was observed in those spectra for short reaction times. This shoulder can be attributed to the presence of the resonance originating from the Ag nanostructures with lower symmetry such as nanowires with a pentagonal profile [23]. As the reaction proceeds from 10 to 120 min the peak positioned at ~350 nm broadens indicating an increase in size and polydispersity.



Figure 22. UV-Vis spectrum of Ag nanoparticles synthesized in ethylene glycol (EG) at a PVP/Ag mole ratio of 1 and 10 minutes of reaction.



Figure 23. UV-Vis spectrum of Ag nanoparticles synthesized in ethylene glycol (EG) at a PVP/Ag mole ratio of 1.7 and 10 minutes of reaction.



Figure 24. UV-Vis spectrum of Ag nanoparticles synthesized in ethylene glycol (EG) at a PVP/Ag mole ratio of 3 and various reaction times.

4.2.3 Morphological Analyses by Scanning Electron Microscopy (SEM)

Figure 25 shows the SEM images of silver particles synthesized at a PVP/Ag molar ratio of 1. The presence of sub-micrometric rods (thickness around 200 nm and 800 nm of length) and irregularly shaped equiaxial particles becomes evident. SEM analyses on the samples synthesized in presence of larger amounts of PVP are not shown because of the extremely low yield and difficulty to remove excess of PVP in the samples.



Figure 25. SEM images of silver particles synthesized at a PVP/Ag molar ratio of 1 and 10 minutes of reaction

4.3 EFFECT OF THE M/Ag MOLE RATIO (M: NaCl, KCl, BaCl₂, FeCl₂ AND CaCl₂)

As mentioned above, the use of inorganic species in the synthesis of silver is expected to promote a shape control and prevent agglomeration of the particles [23]. The shape-control in the silver nanostructures was systematically investigated by evaluating different types and concentration of chloride salts and PVP/Ag mole ratio (1.7/1) in starting solutions.

4.3.1 X-Ray Diffraction Analyses

In order to gain additional insights into the role of anionic species in determining the equilibrium size and shape of silver nanostructures, silver nanoparticles were now synthesized in presence of different metal chloride salts: NaCl, KCl, BaCl₂, FeCl₂ and CaCl₂.

Figure 26 shows the XRD patterns corresponding to the solids synthesized at NaCl/Ag mole ratios of 0.006, (a), and 0.012, (b). The reaction time was 30 minutes and the PVP/Ag mole ratio was fixed at 1.7/1 in both cases. All peaks were assigned to FCC-Ag with an average crystallite size in the 41-44nm range. Interestingly, the peaks corresponding to the (220) and (311) planes were not detected in this case. Moreover, the enhanced intensity of the (200) peak in the sample synthesized at a NaCl/Ag mole ratio of 0.006, suggests a preferential growth along that plane. The enhancement of the (200) peak can be attributed to the formation of silver nanocubes and nanorods [7].



Figure 26. XRD patterns of silver nanoparticles synthesized at NaCl/Ag mole ratios of 0.006/1, (a), and 0.012/1, (b). The reaction temperature and time were 160°C and 30 minutes, respectively in all cases. The PVP/Ag mole ratio was fixed at 1.7/1.

NaCl/Ag Molar Ratio	Average crystallite size (nm)	Standard Deviation
0.006	41.1	4.3
0.012	44.7	7

 Table 4. Average crystallite size of the samples synthesized at various NaCl/ Ag molar ratio. The PVP/Ag mole ratio was 1.7/1 and the concentration of starting silver solution 94 mM.

Figure 27 shows the XRD patterns for the silver powders produced at KCl/Ag molar ratios of 0.001, (a), 0.003, (b), 0.006, (c), and 0.012, (d). PVP/Ag mole ratio was kept constant at 1.7/1 in all experiments. All main diffraction peaks correspond to FCC-Ag. The minor presence of AgCl was detected as suggested by the less intensive diffraction peaks at 2θ values of 32 and 44 degrees.



Figure 27. XRD patterns of silver nanoparticles synthesized at KCl/Ag mole ratios of 0.001/1, (a), 0 .003/1, (b), 0.006/1, (c) and 0.012/1, (d). The reaction temperature and time were 160 °C and 30 minutes, respectively in all cases. The PVP/Ag mole ratio was fixed at 1.7/1.

The presence of this ethylene glycol-insoluble AgCl was more pronounced in those samples synthesized at larger KCl/Ag mole ratios, which is attributed to the larger availability of chloride ions in the reacting solutions. The lattice parameter for the FCC-Ag phase was estimated for all samples and varied between 4.084 Å and 4.090 Å.

Table 5 summarizes the average crystallite sizes estimated for all samples synthesized at various KCl/Ag molar ratios and 30 minutes of reaction. Also in this case, a decrease in the average crystallite size was observed for those samples synthesized at lower KCl/Ag mole ratios; however, this parameter went up to 44 nm when this molar ratio was increased. The increase of the ionic strength in the reacting solutions at larger amounts of the chloride salts could have overcome the steric repulsive interactions provided by PVP species and enhancing crystal growth.

KCl/Ag Molar Ratio	Average Crystallite size (nm)	Standard Deviation
0.001	25	9
0.003	19	3.4
0.006	44	5
0.012	38	1

Table 5. Average crystallite size of the samples synthesized at various KCl/ Ag molar ratio. The PVP/Ag mole ratio was 1.7/1 and the concentration of starting silver solution 94 mM.

The formation of silver nanostructures was also studied in presence of $BaCl_2$, $FeCl_2$ and $CaCl_2$ in starting solutions. The PVP/Ag mole ratio was kept constant at 1.7/1 in all experiments at 160°C. Figure 28 shows the XRD patterns of silver powders synthesized

after 30 minutes and different BaCl₂/Ag molar ratios. Although main peaks corresponded to FCC-Ag phase, less intense peaks of AgCl were observed, which is known to exhibit very low solubility in water and ethylene glycol solutions [32]. The large excess of free chloride ions when BaCl₂ was used should be responsible for the earlier reaction between chloride and silver dissolved species to give insoluble AgCl. Residual silver ions should have been reduced by polyol. The corresponding lattice parameter was estimated at a = 4.080 Å for both samples; this value is in very good agreement with the value for bulk silver (a = 4.0862 Å). The intensity of the peaks (200) increase as the BaCl₂ concentration is increased as shown in Figure 28(c). As suggested earlier, the peak (200) intensity increase suggest formation of nanocubes or nanorods [7], which depends of the process of initial seed formation.



Figure 28. XRD patterns of silver nanoparticles synthesized at BaCl₂/Ag mole ratios of 0.001/1, (a), 0 .003/1, (b) and 0.006/1, (c). The reaction temperature and time were 160 °C and 30 minutes, respectively in all cases. The PVP/Ag mole ratio was fixed at 1.7/1.

As Table 6 shows, the reduction of the crystallite size was significant when a BaCl₂/Ag molar ratio as low as 0.001 was used; the crystallite size did not exhibit a noticeable change at larger BaCl₂/Ag molar ratios. Apparently, the lower availability of free chloride ions (i.e. lower BaCl₂/Ag molar ratios) could have promoted the formation of AgCl leaving fewer amounts of free silver ions to get reduced by the polyol medium.

BaCl ₂ /Ag Molar Ratio	Average Crystallite size (nm)	Standard Deviation
0.001	17	6.1
0.003	42	2
0.006	48	11.3

Table 6. Average crystallite size of the samples synthesized at various BaCl₂/Ag molar ratio. The PVP/Ag mole ratio was 1.7/1 and the concentration of starting silver solution 94 mM.

Figure 29 shows the XRD patterns for the silver powders produced at $FeCl_2/Ag$ molar ratios of 0.001, (a), 0.003, (b), 0.006, (c), 0.012, (d); all XRD peaks corresponds to diffraction peaks of FCC-Ag. Also in this case, a small AgCl peak is observed in Figure 29 (d) contrary to KCl mole ratio in Figure 27 (d). It remains unclear why the presence of cation salts leads to the formation of silver particles [25]. The corresponding lattice parameter in all samples were a = 4.080 Å, which agrees perfectly with the data in the literature [25]. The average crystallite size, estimated by the Scherrer's equation, is shown in table 7. The evident reduced average crystallite size ~19 nm was at FeCl₂/Ag in molar ratio of 0.003/1. Wiley *et. al.* [17] reports the ability of Fe (II) to remove oxygen, it provides a means to control the oxidative etching of silver, which can help to the formation

of nanowires, which Fe (II) could react with and removed the adsorbed atomic oxygen that would otherwise etch twinned seeds and block self-catalytic addition of silver atoms.



Figure 29. XRD patterns of silver nanoparticles synthesized at FeCl₂/ Ag mole ratios of 0.001/1, (a), 0 .003/1, (b), 0.006/1, (c) and 0.012/1, (d). The reaction temperature and time were 160 °C and 30 minutes, respectively in all cases. The PVP/Ag mole ratio was fixed at 1.7/1.

FeCl ₂ /Ag Molar Ratio	Average Crystallite size (nm)	Standard Deviation
0.001	43	3.3
0.003	19	1
0.006	45	8
0.012	34	10

 Table 7. Average crystallite size of the samples synthesized at various FeCl₂/Ag molar ratio. The PVP/Ag mole ratio was 1.7/1 and the concentration of starting silver solution 94 mM.

In turn, the diffraction patterns for the silver powders produced at CaCl₂/Ag mole ratios of 0.001/1, (a), 0.003/1, (b), 0.006/1, (c) and 0.012/1, (d) are shown in Figure 30; the observed peaks were assigned to the (111) and (200) planes in FCC-Ag. Again, AgCl co-existed with FCC-Ag in all samples; the larger the CaCl₂/Ag molar ratio the larger the relative amount of AgCl solid, as suggested by the remarkably enhancement of the corresponding XRD peaks. The preferential growth of the (200) plane was also observed by other groups when silver nanocubes were produced [23]. The lattice parameter of FCC-Ag was estimated at 4.085 Å, which is in good agreement to the value for bulk silver. Table 8 shows the corresponding crystallite size of those samples synthesized at different CaCl₂/Ag molar ratios. The (200) peak evidently increase as a minor amount of concentration of the CaCl₂/Ag (0.001/1) is added to the solution, a decrease of the intensity peak (200) is observed as molar ratio $CaCl_2/Ag$ concentration increase at 0.012/1, which can be due initial seed formation in this case through of the fast formation of AgCl nanocrystals into the solution which can allow low discharge Cl⁻ anions possible in the solution. When a minor amount of $CaCl_2$ as 0.001 - 0.006 is added to the solution it can promote formation of bypiramids or cubes. Since bipyramids are bounded by (100) facets and XRD patterns [figure 30(a-c)] obtained, suggest preferentially orientation of (100) plane parallel to the substrate which suggest this type of formation of cubes or rods in the final product [37]. Since more Cl⁻ anions are added in the solution, as concentration of CaCl₂/Ag molar ratio is considered in a molar ratio of 0.012/1, the increase of the peak of AgCl nanocrystals can suggest a fast formation rate of AgCl not capable to discharge Ag⁺ and Cl⁻ ions to the solution to promote nanocubes formation after 30 minutes of reaction.



Figure 30. XRD patterns of silver nanoparticles synthesized at CaCl₂/ Ag mole ratios of 0.001/1, (a), 0 .003/1, (b), 0.006/1, (c) and 0.012/1, (d). The reaction temperature and time were 160 °C and 30 minutes, respectively in all cases. The PVP/Ag mole ratio was fixed at 1.7/1.

CaCl ₂ /Ag Molar Ratio	Average Crystallite size (nm)	Standard Deviation
0.001	21.3	1
0.003	23	0
0.006	38.6	4
0.012	37.1	0

Table 8. Average crystallite size of the samples synthesized at various CaCl₂/Ag molar ratio. The
PVP/Ag mole ratio was 1.7/1 and the concentration of starting silver solution 94 mM.

4.3.2 UV-Vis Measurements

Figure 31 shows the absorption spectra of silver nanostructures synthesized at a NaCl/Ag molar ratio of 0.006 and different reaction times.



Figure 31. UV-Vis spectra of Ag nanostructures synthesized at a NaCl/Ag mole ratio of 0.006/1 mole ratio and different reaction times. The PVP/Ag molar ratio was 1.7/1.

The PVP/Ag molar ratio was fixed at 1.7/1 in all cases. An evident, though broad, plasmon resonance peak was observed and centered on 400 nm, which is typical of metallic silver [25]. In addition to this main plasmon peak, a shoulder centered on ~355 nm became evident particularly for those samples synthesized at shorter reaction times; the co-existence of this minor shoulder in addition to the main plasmon resonance peak can suggest the formation of elongated structures (e.g. nanorod) [25]. Rycenga *et al* [35] explains that size dependence of localized surface plasmon resonance (LSPR) properties of elongated morphology have two distinct LSPR modes, transverse mode and longitudinal

mode when the aspect ratios greater than 1 but less than 20 such as nanowires, the LSPR longitudinal mode shifts 350 to 460 nm while the transverse mode shows essentially no shift. This shoulder was not observed in those absorption spectra for silver nanostructures synthesized in PVP only.

Figure 32 shows the plasmon resonance spectra of Ag nanostructures synthesized at different reaction times and at a NaCl/Ag molar ratio of 0.012. Also in this case, the minor shoulder at 351 nm suggests the formation of wires or rods in the final products. Moreover, the plasmon peak, initially centered on 390 nm, became broader and red-shifted at prolonged reaction times, suggesting the crystal growth and the increase in the particle size polydispersity.



Figure 32. UV-Vis spectra of Ag nanostructures synthesized at a NaCl/AgNO₃ mole ratio of 0.012/1 mole ratio and different reaction times. The PVP/Ag molar ratio was 1.7/1.

Figure 33 and Figure 34 show the optical absorption spectra corresponding to the silver nanostructures synthesized using a KCl/Ag mole ratio of 0.003 and 0.006 for 30 minutes of reaction.



Figure 33. UV-Vis spectra of Ag powders produced using a KCl/Ag mole ratio of 0.003/1. The reaction time was 30 minutes and the PVP/Ag molar ratio 1.7/1.



Figure 34. UV-Vis spectra of Ag powders produced using a KCl/AgNO₃ mole ratio of 0.006/1. The reaction time was 30 minutes and the PVP/Ag molar ratio 1.7/1.
The most intense and sharp peak is centered on 387-390 nm in both samples. The most remarkable features of these UV-Vis spectra are the presence of shoulders at 347 nm and 357 nm (Figure 33) and 347 nm (Figure 34). As it was discussed before, these shoulders are expected to be developed when elongated nanostructures (wires, rods) have been produced, which is consistent with the XRD information and corroborated by the microscopic analyses shown in the following sections. This strong dependence of the location and intensity of the surface plasmon resonance with shape in metallic nanostructures has been discussed in detail by Wiley *et al.* [37].

All morphologically induced spectral shifts have a tendency on the shape effect of surface polarization which is determined about the weight on a spring of the electrons where its period and amplitude of oscillation, polarization determines the frequency and dipole moment of electron oscillations, and thus the frequency and intensity scattered or absorbed. The effect of well defined silver nanostructures is shown on the plasmon resonance, which is clearly apparent after examination of the UV-Vis extinction spectra [37].

In the case of the silver samples synthesized in presence of different concentrations of BaCl₂, the plasmon peaks were narrow, particularly in that sample synthesized at a BaCl₂/Ag molar ratio as low as 0.001 and 5 minutes of reaction, where it was centered on 421nm (Figure 35). The sharpness of the plasmon peaks indicates the presence of highly monodisperse nanocrystals. The plasmon was also observed in the samples synthesized at a BaCl₂/Ag molar ratio of 0.003 and reaction times of 5 and 10 minutes (Figure 36); however they were red-shifted with respect to the previously commented sample (431 nm), which would be an indicative of the presence of larger silver crystals. This trend in crystal size

was also suggested by the crystallite size estimation from XRD data. The slight but noticeable red-shift of the Plasmon peak by prolonging the reaction time up to 10 minutes is also considered an evidence of the progress of the crystal growth stage along the reaction period. The plasmon peak broadening at larger reaction times could be attributed to the increase in scattering from the larger particles in polydisperse suspensions.

It must be indicated that prolonging the reaction time above 10 minutes was not conducive to any optical response from the samples, which may be attributed to the enhanced formation of insoluble silver chloride. It was also interesting to realize the absence of the shoulders observed in other systems that suggests the absence of elongated morphologies in these samples.



Figure 35. UV-Vis spectra of Ag nanostructures synthesized at a BaCl₂/AgNO₃ mole ratio of 0.001/1 mole ratio at 5 minutes of the reaction. The PVP/Ag molar ratio was 1.7/1.



Figure 36. UV-Vis spectra of Ag nanostructures synthesized at a BaCl₂/Ag mole ratio of 0.003/1 at 5 and 10 minutes of reaction. The PVP/Ag molar ratio was 1.7/1.

The UV-Vis spectrum corresponding to the silver nanostructures synthesized at a FeCl₂/Ag mole ratio of 0.001 and 30 minutes of reaction is shown in Figure 37. An intense plasmon peak was observed around 390nm, which coexisted with two minor shoulders at 350 nm and 353 nm. Again, these small shoulders are attributed to the formation of particles with low symmetry like rods or wires, whose longitudinal plasmon resonance caused the optical absorption at lower wavelengths [23, 25]. The spectrum of Figure 38 corresponds to the silver powders synthesized at a FeCl₂/Ag molar ratio of 0.006 and different reaction times. The main plasmon peak, centered on 380 nm, was also clearly observed in the spectrum of the sample synthesized at 30 minutes. The small shoulder at 351 nm was also observed. As stated before, this shoulder is attributed to the elongated shape of the crystals. However, the absorption spectra become broader by prolonging the reaction time, which suggests the increase in the polydispersity of the particle size in these samples.



Figure 37. UV-Vis spectra of Ag powders produced at FeCl₂/AgNO₃ mole ratios of 0.001/1. The reaction time was 30 minutes and the PVP/Ag molar ratio 1.7/1.



Figure 38. UV-Vis spectra of Ag powders produced at FeCl₂/AgNO₃ mole ratios of 0.006/1. The PVP/Ag molar ratio 1.7/1.

Silver nanostructures were also synthesized at CaCl₂/Ag molar ratios of 0.001 (Figure 39) and 0.012 (Figure 40). In the first case, a broad main peak at 470 nm and shoulders at 392 nm and 347 nm, were observed. The broadening in the main surface plasmon resonance peak was attributed to the polydispersity in length and width of as-synthesized nanowires [39]. The presence of the two shoulders, one with higher absorption than the other, was also in this case, attributed to the decreasing symmetry of the wires cross section [38, 39]. On the other hand, the UV-Vis spectrum for the sample synthesized at higher CaCl₂/Ag molar ratio, exhibited a well defined plasmon centered on 380 nm and one absorption shoulders to the formation of Ag nanostructures with lower symmetry, e.g. nanowires, but now exhibiting a pentagonal cross section.



Figure 39. UV-Vis spectra of Ag powders produced at CaCl₂/AgNO₃ mole ratios of 0.001/1. The reaction time was 30 minutes and the PVP/Ag molar ratio 1.7/1.



Figure 40. UV-Vis spectra of Ag powders produced at CaCl₂/AgNO₃ mole ratios of 0.012/1. The reaction time was 30 minutes and the PVP/Ag molar ratio 1.7/1.

4.3.3 Morphological Analyses

TEM and SEM analyses were performed onto produced samples in order to confirm the morphologies expected from XRD and UV-Vis measurements. As Figure 41 evidences, silver structures synthesized at a NaCl/Ag molar ratio of 0.012 consisted of nanoparticles of varied shapes including twinned and elongated nanoparticles such as nanorods, which were predominant. This morphological features were in good agreement with the information provided by UV-Vis measurements.



Figure 41. TEM images of silver nanostructures produced using a NaCl/AgNO₃ mole ratio of 0.012/1 and 10 minutes of reaction time. The PVP/Ag mole ratio was 1.7/1.

FE-SEM images of the samples synthesized at different KCl/Ag molar ratios are shown in Figure 42. In excellent agreement with the information provided by UV-Vis measurements, these images confirmed the actual formation of wires with thickness in the 50-170 nm range in almost all samples. Elemental analyses by XEDS analyses evidenced the presence of silver and chloride species in the spherical particles, which is attributed to the presence of insoluble AgCl, suggested by XRD measurements. The co-existence of AgCl with silver nanostructures has also been observed by M.Tsuji *et al.* [32] and was attributed to the concentration of free chloride species in solution. The increase of the KCl/Ag molar ratio up to 0.012 promoted the formation of thicker rods (Figure 42d). The morphologies and high aspect ratios in as-synthesized silver nanowires can be explained in terms of the adsorption of chloride species onto specific crystallographic planes, inhibiting their development while favoring the preferential growth of another ones, (111) or (200) in our case [5, 17, 23, 31-32]. M.Tsuji *et al.* [32] also proposed the formation of triangular

particles, which was also observed, although in very less amounts, in our samples synthesized at a KCl/Ag molar ratio of 0.012.



Figure 42. FE-SEM images of silver nanostructures synthesized at 30minutes of reaction mixture and KCl/AgNO₃ mole ratios of (a), 0.001/1; (b), 0.003/1; (c), 0.006/1 and (d), 0.012/1. The PVP/Ag molar ratio was fixed at 1.7/1.

Figure 43 shows the TEM image of the highly monodisperse, twined and equiaxial nanoparticles synthesized in presence of BaCl₂. The high monodispersity in particle size was in excellent agreement with our previous expectation coming from UV-Vis analyses.



Figure 43. TEM image of highly monodisperse silver nanoparticles produced using a BaCl₂/Ag molar ratio of 0.001 mole ratio at 5 minutes of reaction time. The PVP/Ag molar ratio was 1.7/1. The average diameter of the particles was about 50nm.

TEM images of Figure 44 correspond to the silver solids synthesized in presence of FeCl₂ at different FeCl₂/AgNO₃ mole ratios in the 0.001/1 - 0.012/1 range. Figure 44(a) evidenced the formation of 70 nm thick silver nanowires after 30 minutes of reaction when a FeCl₂/AgNO₃ mole ratio of 0.001/1 was used. Increasing the molar ratio to 0.003/1, Figure 44(b), was conducive to the formation of 45 nm-thick and 100 nm-length nanorods after a reaction time as short as 10 minutes. Moreover, increasing the FeCl₂/AgNO₃ mole ratio up to 0.012/1 promoted the formation of thick bars, although more disperse in thickness and length (Figure 44-c).

Evidently, the morphology of silver nanostructures will strongly depend on the relative amount and type of the chloride salt used into the solution. The adsorption of chloride and iron ions onto particular crystallographic planes in the silver particles should have promoted the preferential longitudinal growth of the crystals.



Figure 44. TEM images of silver nanostructures synthesized at different reaction times and FeCl₂/AgNO₃ mole ratios. (a) 10 minutes, 0.001/1; (b) 30 min, 0.003/1 mole ratio, and (c) 120 minutes, 0.012/1. The PVP/Ag molar ratio was fixed at 1.7/1.

The morphological features of the silver structures formed in presence of $CaCl_2$ were also investigated. Figure 45(a) shows the FE-SEM and TEM images of the silver particles morphologies synthesized at $CaCl_2/Ag$ molar ratios of 0.001 (a) and 0.006 (b). As seen,

lower amounts of chloride species was conducive to the formation of nanocubes and triangular bi-pyramidal crystals. On the contrary, very thin silver nanowires were formed when a CaCl₂/Ag molar ratio of 0.006 was used. The inset of Figure 45(b) corresponds to the electron diffraction (ED) pattern, indexed to single crystal Ag along the [011] zone axis in agreement with the JCPDS card No. 89-3722. The UV-Vis measurements of these samples clearly suggested the presence of elongated shapes, a fact that was corroborated by the TEM analyses. Sometimes, rods were found to be non-straight. An example is shown of Figure 46(a). HRTEM images showing the region where the change of direction takes place are displayed in Figure 46(b). A change in direction during synthesis does not alter the growth direction along the [111] direction.



Figure 45. (a) FE-SEM image of silver particles synthesized at CaCl₂/Ag molar ratio of 0.001; (b) TEM image showing Ag rods and wires produced at a CaCl₂/Ag mole ratio of 0.006. The reaction time was 30 minutes and the PVP/Ag molar ratio 1.7/1. The inset shows a typical electron diffraction pattern taken from any individual nanowire by directing the electron beam perpendicularly.



Figure 46. (a) TEM image of a non straight silver rod synthesized at a CaCl₂/Ag molar ratio of 0.001;
(b) HRTEM images showing the region where the change of direction takes place. The reaction time was 30 minutes and the PVP/Ag molar ratio was fixed at 1.7/1.

In summary, the shape-controlled growth of silver particles was successfully achieved in polyol medium in presence of chloride salts and PVP. The different morphologies were strongly dependent on the type and concentration of the chloride salts in ethylene glycol, and the reaction time. The next step of the present research addresses the evaluation of the silver nanorods and nanowires suspended in ethylene glycol from the point of view of the thermal conductivity in the so-called nanofluids. Also, the effect of the volumetric loading on the thermal conductivity of nanofluids bearing those metallic particles will be investigated.

4.4 EFFECT OF SILVER LOADING AND SHAPE ON THE THERMAL CONDUCTIVITY COEFFICIENT IN ETHYLENE GLYCOL-BASED NANOFLUIDS

The thermal conductivity measurements were carried out using the hot-wire method where the coefficient of thermal conductivity (k) is calculated from a temperature change of the platinum wire with time and the enhancement percent (%) indicates variation of experimental value of the silver nanofluid in comparison to the value of k in ethylene glycol. The data are used to calculate the effective thermal conductivity of the nanofluid via an analytical solution of Fourier's equation. In our measurements, k enhancement was reasonably increased in nanofluids containing 15% v/v of silver rods and wires in Ethylene Glycol.

Nanofluids containing silver nanorods (NaCl/Ag molar ratio of 0.012) and nanowires (KCl/Ag molar ratio of 0.003) were selected and prepared at various volumetric loadings in the 0-15% range. Table 9 and Table 10 summarize the attained results. Each measurement was run by duplicate or triplicate. Evidently, there was a moderate but noticeable increment in the thermal conductivity and the corresponding efficiency in those nanofluids at larger volumetric loadings of silver nanostructures. In the case of nanorods (Table 9), a low volumetric loading was conducive to a decrease in the thermal conductivity (from 0.290 to 0.280 W/m*K), which can be due to the nanosize thickness and low fraction of silver wires. Teja *et al.* [42] also reported decreasing in thermal conductivity in silver nanofluids by the particle size, although his results were not conclusive. In turn, the efficiency was enhanced in the 101-122% range, with respect to bare ethylene glycol, at

volumetric loadings above 10%. The thermal conductivity was increased up to 0.335 ± 0.02

W/m*K for a volumetric load of 15%.

ratio of 0.012.						
Parameter	Pure Ethylene Glycol (Sigma Aldrich)	Silver nanorods in Ethylene Glycol 5 v/v%	Silver nanorods in Ethylene Glycol 10 v/v%	Silver nanorods Ethylene Glycol 15 v/v%		
Thermal Conductivity Coefficient (W/m*K)	0.290	0.280±0.002	0.293±0.004	0.335±0.02		
Enhancement (%)	100	96.5	101.7	122.4		

Table 9. Average thermal conductivity coefficient and enhancement percent of effective thermal
conductivity of ethylene glycol-based nanofluids bearing nanorods synthesized at a NaCl/Ag molar
ratio of 0.012.

A similar trend was observed in those nanofluids bearing thinner silver nanowires synthesized in presence of KCl (Table 10); however, the increase in thermal conductivity coefficient was less than the value obtained in the nanofluids bearing silver nanorods. In addition to the nanometric nature of these wires, another factors including residuals of surfactant or agglomeration, can also explain the low increase in thermal conductivity [8, 10, 43, 45, 47-51].

Table 10. Average thermal conductivity coefficient and enhancement percent of effective thermal conductivity of ethylene glycol-based nanofluids bearing nanowires synthesized at a KCl/Ag molar ratio of 0.003.

Parameter	Pure Ethylene Glycol (Sigma Aldrich)	Silver nanowires in Ethylene Glycol 5 v/v%	Silver nanowires in Ethylene Glycol 10 v/v%	Silver nanowires Ethylene Glycol 15 v/v%		
Thermal Conductivity Coefficient (W/m*K)	0.290	0.286 ± 0.003	0.275±0.002	0.330±0.004		
Enhancement (%)	100	99.368	94.270	115.2		

Velasco et al. [29] reported an increase in thermal conductivity of 32% on 21 nm -Cu bearing nanofluids at a 0.3 v/v % in ethylene glycol using size control for its particle as parameter of study and no shape control. He reported that an enhancement in thermal conductivity is strongly dependent on volumetric concentration of the nanoparticles in the fluid, and the inter particle length could be related to the observed enhancement of the thermal conductivity and must be considered as an important factor in which thermal conductivity can be affected. Also, an agglomeration of the particles was observed in his results which can be another variant in his results.

The discrepancy with our results can be explained by the difference between this variation of shape and length elongated silver particles that should affect the interparticle length, which in turn would influence on the number of particle collisions, the probable contamination of the base fluid by using of PVP as stabilizing agent. The sensitivity of the corresponding experimental set-up used for the measurement of the thermal conductivity coefficient could also be involved with observed discrepancies.

5 CONCLUSIONS AND FUTURE WORK

Silver nanostructures have been successfully synthesized in ethylene glycol in presence of PVP as a growth inhibitor. A PVP/Ag molar ratio of 1.7 was selected as the optyimum to attain a reasonably good control on the size of silver nanoparticles; the average crystallite size was estimated at 40nm.

The capability to modify the silver crystal habit and, hence, the final particle shape, was achieved by controlled addition and selection of the source of chloride species (NaCl, KCl, BaCl₂, FeCl₂ and CaCl₂). The UV-vis spectra of the silver nanostructures synthesized in presence of NaCl, KCl, FeCl₂ and CaCl₂ evidenced the presence of the main Plasmon peak but co-existing with small shoulders which could be attributed to the formation of particles with low symmetry like rods or wires. SEM and TEM analyses confirmed the formation of elongated, wire-shaped particles. Chloride ions should have been adsorbed onto specific crystal planes inhibiting their growth while promoting the development of others.

The thermal conductivity was increased from 0.290 W/m*K for pure ethylene glycol up to 0.335±0.02W/m*K for a volumetric load of 15% of silver nanorods in ethylene glycol. The same coefficient was increased up to 0.330±0.004 W/m*K in presence of thin silver nanowires. The interparticle collisions, promoted at higher volumetric loadings, can be related to the observed increase in the thermal conductivity coefficient. On the other hand, probable contamination of the base fluid with PVP adsorbed on the silver rods and wires, could also explain the modest enhancement of the thermal conductivity coefficient.

Future work will be focused on the synthesis of different salts to investigate the actual effect if the cations and anions on the final size and shape of the silver nanostructures.

The electrical conductivity of the different silver nanostructures is also worth to be investigated in the forthcoming experimental work.

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