PROJECT TITLE: High Accuracy Photopyroelectric Calorimetry for Magnetic Nanofluids
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Progress Report 6

General Objective: Behaviour of the static and dynamic thermal parameters of magnetic nanofluids as a function of type and size of nanoparticles.

1.PPE measurements of thermal diffusivity and effusivity of magnetic nanofluids with different type and size of nanoparticles.

In this report we investigate the influence of type and size of nanoparticles on the thermal parameters of some magnetic nanofluids. Two types of carrier liquids (transformer oil and polypropylene glycol) have been combined with two types of magnetic nanoparticles (Fe_3O_4 and $MnFe_2O_4$). The resulting magnetic nanofluids were investigated by using the two well-known PPE detection configurations: (i) the back (BPPE) detection, combined with the thermal-wave-resonator-cavity (TWRC) scanning procedure was used for thermal diffusivity measurements; (ii) the front (FPPE) configuration, together with the frequency scanning technique was used for thermal effusivity investigations. In both detection configurations the information was contained in the phase of the PPE signal.

Concerning the synthesis of the nanofluids, hydrophobic monodispersed iron oxide (Fe_3O_4) and manganese ferrite ($MnFe_2O_4$) nanoparticles were synthesized by high-temperature organic solution phase method. The reaction of metal precursors, iron acetylacetonate $Fe(acac)_3$ and mangan acetylacetonate $Mn(acac)_2$ with hydrophobic stabilizer like oleic acid and oleylamine in a high boiling point solvent, benzyl ether, could lead monodispersed magnetic nanoparticles with controlled size and shape. The size of the particles is tuned by varying the concentration of the metal precursors, while the shape is controlled by the amount of the stabilizer added to reaction mixture.

In a typical synthesis procedure, 2.28 g (6.4 mmol) of iron (III) acetylacetonate and 1.62 g (6.4 mmol) mangan (II) acetyl acetonate were mixed with 5 ml (4.45 g) oleic acid and different quantities of oleylamine in 40 ml dibenzylether. The iron (III) acetylacetonate or mangan (II) acetyl acetonate to oleic acid molar ratio was 1: 2.5, while the molar ratio of oleic acid to oleylamine was adjusted in order to obtain different size and shape magnetic nanoparticles. All reaction conditions are summarized in Table 1. First the solution was heated to 200^0C under argon atmosphere and vigorous stirring. After 1 h, the solution was heated to reflux and keep at this temperature for 1 h. Finally the solution was cooled down, washed several times with a mixture of ethanol and hexane, separated magnetically and re-dispersed in toluene or other carrier solvent.

Table 1. Summary of reaction conditions

Sample	$Fe(acac)_3$/ $Mn(acac)_2$: oleic acid (molar ratio)	Oleic acid:oleylamine (molar ratio)	Size (nm)	Shape
Fe_3O_4-a	1: 2.5	1: 2	10	spherical
Fe_3O_4-b	1: 2.5	2:1	20	octahedral
Fe_3O_4-c	1: 2.5	1:0	50	cubic
$MnFe_2O_4$-a	1: 2.5	1: 2	10	spherical
$MnFe_2O_4$-b	1: 2.5	2:1	35	octahedral
$MnFe_2O_4$-c	1: 2.5	1:0	80	cubic

A synthesis of the results obtained for the two measured thermal parameters, thermal diffusivity and effusivity for all the combinations polypropylene glycol/transformer oil and $MnFe_2O_4/Fe_3O_4$ are presented in Table 2.

Table 2. Room temperature values of thermal diffusivity and effusivity for the combinations polypropylene glycol/transformer oil and $MnFe_2O_4/Fe_3O_4$ as obtained from PPE investigations.

Magnetic nanofluid		Thermal diffusivity x10^{-8} (m^2s^{-1})	Thermal effusivity ($Ws^{1/2}m^{-2}K^{-1}$)
ppg		7.69 ± 0.30	619 ± 4
tr. oil		6.77 ± 0.28	543 ± 4
ppg + $MnFe_2O_4$	size: 10 nm	7.45 ± 0.24	528 ± 4
	size: 20 nm	7.48 ± 0.22	491 ± 4
	size: 80 nm	7.43 ± 0.30	457 ± 3
ppg + Fe_3O_4	size: 10 nm	7.67 ± 0.31	595 ± 4
	size: 35 nm	7.59 ± 0.26	591 ± 4
	size: 50 nm	7.43 ± 0.30	582 ± 4
tr. oil + $MnFe_2O_4$	size: 10 nm	6.60 ± 0.20	524 ± 4
	size: 20 nm	6.58 ± 0.22	514 ± 4
	size: 80 nm	6.47 ± 0.35	412 ± 4
tr. oil + Fe_3O_4	size: 10 nm	6.35 ± 0.22	530 ± 4
	size: 35 nm	6.14 ± 0.30	512 ± 3
	size: 50 nm	6.09 ± 0.36	437± 2

2.Complementary methods for magnetic nanofluid characterization.
Investigation of the morphology of the structures and nanoparticles' size distribution.

TEM images of the as-synthesized iron oxide and manganese ferrite for different samples prepared in different reaction conditions show that for the ratio 1:2 oleic acid oleylamine, spherical nanoparticles of about 10 nm size were obtained (see Figure 1: Fe_3O_4-a, $MnFe_2O_4$-a). For intermediary molar ratio of 2:1, quasi regular octahedral shape nanoparticles of 20 to 30 nm were obtained (see Figure 1: Fe_3O_4-b, $MnFe_2O_4$-b). When just oleic acid is used for stabilizing the magnetic nanoparticles larger cubic nanoparticles of 60 to 80 nm were obtained (see Figure 1: Fe_3O_4-c, $MnFe_2O_4$-c). So, it is to notice that the size of the nanoparticles increases with the decreasing of the relative concentration of oleylamine. It should also be pointed out that the particles larger than 10 nm showed gradually octahedral and finally cubic shape when they are synthesized in a reaction mixture containing smaller concentration of oleylamine (octahedral shape) and no oleylamine, the cubic shape. This demonstrates the strong effect of the oleic acid/oleylamine molar ratio on the nanocrystals growth rate due to the different binding ability of the two stabilizers onto crystal facets.

Data analysis, correlation with physico-chemical processes and PT investigations

Concerning the PPE investigations, the main results are listed in Table 2. As a general conclusion, the presence of the nanoparticles, for this concentration range, decreases the value of the thermal parameters of pure carrier liquids and both thermal diffusivity and effusivity decrease with increasing nanoparticles size, independently on the carrier liquid. As an order of magnitude, the influence of the nanoparticles size is more pronounced for the thermal effusivity (maximum relative change 24%) compared with thermal diffusivity (maximum relative change 7%).

We have to point out that this decrease of the values of dynamic thermal parameters of the nanofluids due to the presence of the nanoparticles is valid only at these lower concentrations (about 50 mg/ml). At much higher concentrations of nanoparticles (150 mg/ml ï 350 mg/ml) the values of the thermal parameters of the nanofluids increase compared with the pure carrier liquid and increase with increasing nanoparticles concentrations. At higher nanoparticles concentration the explanation is clear due to the values of the nanoparticlesô thermal parameters which are higher than those of the carrier liquids. However, it is well-known that in the case of binary liquid mixtures (especially when the liquids are associative) or liquid/solid mixtures (when the solid component forms chain structures) the behaviour of the thermal parameters with the composition is usually nonlinear (presenting a minimum at a given concentration, or a percolation threshold due to the fact that the additivity rule is not respected). This seems to be the case of the investigated nanofluids: at low nanoparticlesô concentration, the value of the nanoparticleôs thermal parameter is not important yet (has no contribution to the value of the nanofluidôs total thermal parameter) but their structure disturbs the thermal conduction in the fluid. For higher nanoparticles concentrations, the values of the thermal parameters of the nanoparticles themselves start to influence the thermal conduction and the values of the thermal parameters of the nanofluid increase with increasing nanoparticles concentration.

Indexes of performance (stage 6)

ISI journals

1.Photothermoelectric (PTE) Detection of Phase Transitions. Application to Triglycinesulphate (TGS), D. Dadarlat, C. Tudoran, V. Surducan, C. Bourgès, P. Lemoine, E. Guilmeau, Thermochimica Acta 624 21ï 26 (2016)

2. Thermophysical properties of masonry units: accurate characterization by means of photothermal techniques and relationship to porosity and mineral composition, N. Cobarzan, A.A. Balog, B. Belean, G. Borodi, D. Dadarlat, M. Streza, Construction & Building Materials, 105, 297-306 (2016)

3.Photothermoelectric (PTE) Versus Photopyroelectric (PPE) Detection of Phase Transitions, D. Dadarlat, E. Guilmeau, A. Hadj Sahraoui, C. Tudoran, V. Surducan, C. Bourgès, P. Lemoine, Int J Thermophys 37:53 (pg 1-7) (2016)

4. Rapid, non-destructive determination of butter adulteration by means of photopyroelectric (PPE) calorimetry, L. Cuibus, D. Dadarlat, M. Streza, F. V. Dulf, Z. Diaconeasa, C. Socaciu, J. Therm. Analysis Calorimetry ï DOI 10.1007/s10973-016-5630-4

5. Photopyroelectric Characterization of Magnetic Nanofluids. Influence of Type and Size of Nanoparticles on the Thermal Parameters, D. Dadarlat, I. Craciunescu, R. Turcu, C. Tripon, Thermochimica Acta- submitted

International conferences

1.ñOptothermal characterization of liquid thermoelectricsò, D. Dadarlat, "Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies", 25 - 28 august 2016, Constanta, Romania ï invited

2.ñCombined Photothermal Techniques for Thermal Characterization of Liquid Thermoelectricsò, D. Dadarlat, M. Depriester, K. Touati, A. Hadj Sahraoui, 3rd Conference on Photoacoustic and Photothermal Theory and Applications (CPPTA), 13-16 septembrie 2016, Warsaw, Poland

3.Photopyroelectric Characterization of Magnetic Nanofluids. Influence of Type and Size of Nanoparticles on the Thermal Parametersòò, D. Dadarlat, I. Craciunescu, R.Turcu, C. Tripon, 3rd Conference on Photoacoustic and Photothermal Theory and Applications (CPPTA)ò, 13-16 septembrie 2016, Warsaw, Poland.

Detailed results of this stage can be found in Research Report 6 (Romanian) and in the above mentioned disseminated papers.