PROJECT TITLE: High Accuracy Photopyroelectric Calorimetry for Magnetic Nanofluids
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Progress Report 5

General Objective: PPE calorimetry for thermal effusivity investigation of magnetic nanofluids.

1. **Behaviour of the static and dynamic thermal parameters of magnetic nanofluids as a function of concentration of nanoparticles**

1.1.Preliminary measurements on liquids with known thermal properties.

This section contains some results obtained on water which is a liquid with known thermal properties and used as carrier liquid in many types of nanofluids. All investigations have been performed at room temperature and, as detection configurations, those used later for nanofluid investigations, have been selected: (i) the thermal diffusivity was measured in BPPE-TWRC technique and the obtained results were: 13.6 x$10^{-8}m^2/s$ from the information obtain in the phase of the signal and 13.4 x$10^{-8}m^2/s$ from the information obtain in the amplitude; the results are in agreement which literature data.(ii) the thermal effusivity was measured in the FPPE-TWRC configuration, using water both as backing material as well as coupling fluid. The result for the value of thermal effusivity was 1540 $Ws^{1/2}m^{-2}K^{-1}$, in agreement with literature data.

1.2.PPE measurements of thermal diffusivity and effusivity of magnetic nanofluids with different nanoparticles concentration.

In this report two PT techniques have been used in order to characterize magnetic nanofluids: PPE and for comparison PTE. In both cases, the same experimental setup has been used. The pyroelectric sensor was a single crystal $LiTaO_3$ (0.5 mm, and 0.215 mm thickness - depending on the configuration ï and 1.5x1.5 cm^2 area. The PTE sensor consists of high density sintered pellets (15 mm diameter and 460 εm thickness) of TiS3 with a Seebeck coefficient of about ī600 εV・Kī1. Both sensors were provided with gold electrodes on both faces.

The liquid samples were magnetic nanofluids with transformer oil as the carrier liquid, oleic acid as the surfactant, and Fe3O4 nanoparticles. They have been investigated as a function of the nanoparticlesô concentration, in the range of 0 to 0.623 mg Fe3O4/ml fluid. The synthesis procedure for hydrophobic magnetite nanoparticles *(*Fe3O4・OA*)* involves the co-precipitation (at 80 ŬC) of magnetite from aqueous solutions of Fe3+ and Fe2+ ions in the presence of a concentrated NH4OH solution (25 %) followed by chemisorption of oleic acid (80 ŬC to 82ŬC) on the magnetite nanoparticles. After several steps of purification and elimination of excess oleic acid, the hydrophobic Fe3O4・OA nanoparticles are dispersed in transformer oil at the required concentration.

The results obtained for the thermal parameters are presented in Tables 1 and 2.

Table 1

sample	Thermal effusivity ($Ws^{1/2}$ $m^{-2}K^{-1}$)	Thermal effusivity ($Ws^{1/2}$ $m^{-2}K^{-1}$)
	PTE phase	PPE phase
0.156 mg(Fe_3O_4)/ml fluid	450	460
0.312 mg(Fe_3O_4)/ml fluid	480	480
0.623 mg(Fe_3O_4)/ml fluid	520	530

Table 2

sample	Thermal diffusivity x10^8 (m^2s^{-1})	Thermal diffusivity x10^8 (m^2s^{-1})	Thermal diffusivity x10^8 (m^2s^{-1})
	PTE phase	PTE amplitude	PPE phase
Transformer oil	9.06±0.6	8.72±0.6	9.14±0.4
0.156 mg(Fe_3O_4)/ml fluid	9.33±0.3	8.73±0.4	9.48±0.2
0.312 mg(Fe_3O_4)/ml fluid	9.70±0.7	9.02±0.5	10.22±0.3
0.623 mg(Fe_3O_4)/ml fluid	9.84±0.5	10.38±0.4	10.33±0.5

1.3.Analysis of the results

Small increases of the thermal diffusivity (from9.06×10^{-8} $m^2 \cdot s^{-1}$ up to 9.84×10^{-8} m^2s^{-1}, if using the phase of the signal and from 8.72×10^{-8} m^2s^{-1} up to 10.38×10^{-8} m^2s^{-1}, if using the amplitude) with increasing concentration of Fe3O4 nanoparticles (from 0 up to 0.623 mg Fe3O4/ml fluid) were observed. Similar small increase of the thermal effusivity from 450 $Ws^{1/2}m^{-2}K^{-1}$ up to 520 $Ws^{1/2}m^{-2}K^{-1}$ in the same nanoparticlesô concentration range, was found.

This increase of the values of the thermal parameters with increasing nanoparticles concentration can be attributed to higher values of the nanoparticlesô thermal parameters as compared with those of the carrier liquid.

2. Complementary methods for magnetic nanofluid characterization.

The preparation of magnetic nanofluids with suitable properties for successful applications involves optimizing synthesis methods of magnetic nanoparticles coated with surfactants and their characterization through advanced techniques in order to determine the correlation between the nanostructure and properties.

The properties of magnetite nanoparticles (mean sizes in the range 7-15 nm) stabilized with either hydrophobic layer of oleic acid and oleylamine or with hydrophilic layer of glycerol phosphate have been investigated by magnetization measurements and X-ray Photoelectron Spectroscopy (XPS).

The coating of magnetite nanoparticles with different surfactants was evidenced by XPS spectra. The XPS analysis provides information concerning the element composition (atomic concentration) of the materials surface, as well as the chemical state of the emitting atoms (valence states, oxidation degree, etc.). The element composition of the magnetite nanoparticles coated with surfactants was inferred from the areas delimited by the photoelectron peaks. The chemical state of the atoms relates to the chemical shifts of the peaks with respect to the elemental state, induced by the chemical surrounding of the atoms. Chemical shift represents a change in the binding energy of a core electron of an element due to a change in chemical bonding of that element. Using the appropriate software Casa XPS the peaks have been deconvoluted into the components, each component corresponding to a particular bond type.

The magnetization curves at room temperature for all investigated magnetite nanoparticles covered with surfactants show superparamagnetic behavior and saturation magnetization values in the range 60-73 emu/g. These characteristics demonstrate the potential applications of these biocompatible nanoparticles for biomedicine.

Indexes of performance (stage 5)

ISI journals

1. Thermal characterization of II-VI binary crystals by photopyroelectric calorimetry and infrared lock-in thermography, K. Strzağkowski, M. Streza, D. Dadarlat, A. Marasek, J. Therm. Analysis Calor. 119:319ï327 (2015); DOI 10.1007/s10973-014-4137-0

2. Complementary photothermal techniques for complete thermal characterization of porous or semi-transparent solids, D. Dadarlat, M. Streza, O. Onija, K. Strzalkowski, C. Prejmerean, L. Silaghi-Dumitrescu, N. Cobirzan, J. Therm. Analysis Calor. 119:301ï308 (2015); DOI 10.1007/s10973-014-4091-x

3. Thermoelectrics (TE) used as detectors of radiation. An alternative calorimetry based on the photothermoelectric (PTE) effect. D. Dadarlat, P. R. N. Misse, A. Maignan, E. Guilmeau, M. Depriester, M. Kuriakose, A. Hadj Sahraoui, *Proc. SPIE* 9258, Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies VII, 92582R (February 21, 2015); doi:10.1117/12.2065491;

4. Alternative Calorimetry Based on the Photothermoelectric (PTE) Effect: Application to Magnetic Nanofluids, D. Dadarlat · P. R. N. Misse · A. Maignan · E. Guilmeau · R. Turcu · L. Vekas · C. Tudoran · M. Depriester · A. Hadj Sahraoui, Int J Thermophys DOI 10.1007/s10765-015-1855-x

5. Thermal characterization of ZnBeMnSe mixed compounds by means of photopyroelectric and lock-in thermography methods, K. Strzağkowski, D. Dadarlat, M. Streza, J. Zakrzewski, Applied Physics A 119**,** 1165ï1171 (2015) DOI 10.1007/s00339-015-9086-3

6. Non-destructive Measurement of Total Carotenoid Content in Processed Tomato Products: Infrared Lock-In Thermography, Near-Infrared Spectroscopy/Chemometrics, and Condensed Phase Laser-Based Photoacousticsð Pilot Study, D. Bicanic, M. Streza, O. Dóka, D. Valinger, S. Luterotti, Zs. Ajtony, Z. Kurtanjek, D. Dadarlat, Int J Thermophys DOI 10.1007/s10765-015-1895-2

International conferences

1. Photothermoelectric (PTE) detection of phase transitions. Application to triglycinesulphate (TGS), D. Dadarlat, C. Tudoran, V.Surducan, P. Misse, E. Guilmeau, 44th Winter School on Wave and Quantum Acoustics, Szczyrk, Poland, 02-06 March, 2015

2. Simultaneous measurement of thermal diffusivity and Seebeck coefficient for thermoelectrics by lock-in thermography, M. Streza, M. Depriester, , E. Guilmeau, D. Dadarlat, K. Strzalkowski, 44th Winter School on Wave and Quantum Acoustics, Szczyrk, Poland, 02-06 March, 2015

3. Photopyroelectric Calorimetry. Basics and Recent Developments, D. Dadarlat, International Summer School ĂPhotothermal and photoacoustic instrumental techniquesò, Novi Sad, Serbia, 4-6 Sept. 2015. ï invited lecture

4. Photothermoelectric (PTE) versus Photopyroelectric (PPE) Detection of Phase Transitions, D. Dadarlat, E. Guilmeau, A. Hadj Sahraoui, 18-th Int. Conf. on Photoacoustic and Photothermal Phenomena (ICPPP18), Novi Sad, Serbia, 6-10 Sept. 2015

5. Thermal properties of masonry units and their relation to porosity and mineralogical content, N. Cobirzan, A.A. Balog, D. Dadarlat, B. Belean, M. Streza, 18-th Int. Conf. on Photoacoustic and Photothermal Phenomena (ICPPP18), Novi Sad, Serbia, 6-10 Sept. 2015

6. Detection of phase transitions by using contact photothermal techniques, D Dadarlat, C Tudoran and V Surducan, PIM, Cluj-Napoca, 24-26 Sept., 2015

Detailed results of this stage can be found in Research Report 5 (Romanian) and in the above mentioned disseminated papers.