PHYSICS AND CHEMISTRY OF SOLID STATE
V. 25, No. 1 (2024) pp. 142-147

Section: Physics

DOI: 10.15330/pcss.25.1.142-147

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 1 (2024) С. 142-147

Фізико-математичні науки

PACS: 33.20.Ea, 61.05.C-, 68.37.Hk, 73.63.Fg, 87.64.Je

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

R.G. Abaszade[1,2], E.M. Aliyev[3], A.G. Mammadov[1], E.A. Khanmamadova[1], A.A. Guliyev[1], F.G. Aliyev[2], R.I. Zapukhlyak[4], H.F. Budak[5], A.E. Kasapoglu[5], T.O. Margitych[6], A. Singh[7], S. Arya[7], E. Gür[8], M.O. Stetsenko[9]

Investigation of thermal properties of gadolinium doped carbon nanotubes

[1]Azerbaijan State Oil and Industry University, Baku, Azerbaijan, abaszada@gmail.com,
[2]Azerbaijan University of Architecture and Construction, Baku, Azerbaijan, abaszada@gmail.com,
[3]University of Birmingham, Edgbaston, United Kingdom, e.aliyev@bham.ac.uk,
[4]Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, kotsuybynsky@gmail.com,
[5]Eastern Anatolia High Technology Application and Research Center Office, Erzurum, Turkey, hfeyzi.budak@atauni.edu.tr, aemre.kasapoglu@atauni.edu.tr,
[6]Kyiv Institute for Nuclear Research, National Academy of Sciences of Ukraine, Kyiv, Ukraine, margtanya@gmail.com,
[7]Department of Physics, University of Jammu, Jammu, India, snp09arya@gmail.com,
[8]Eskisehir Osmangazi University , Eskisehir, Turkey, emregur@ogu.edu.tr,
[9]Key Laboratory of Optoelectronic Devices and Systems, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen, PR China, stetsenkomax@gmail.com

Thermal properties characterizations for 10% and 15% Gd doped multi wall carbon nanotubes (MWCNTs) were investigated. The thermal and structural characteristics were investigated using TGA/DSC and TEM techniques. Mass loss characteristics for the synthesized nanocomposite carbon-based nanomaterials were analyzed. It was observed that the specific heat capacity of the studied samples increased proportionally with the increase in temperature.

Keywords: gadolinium, arc discharge method, MWCNT, TEM, TGA, specific heat capacity.

Received 23 December 2023; Accepted 26 February 2024.

Introduction

Doped MWCNT has strong interest for sensors and bioimaging applications. The perspective area of carbon nanomaterials investigation is focused on incorporation different materials to obtain a new nanocomposite with more significant properties. Multiwalled carbon nanotubes (MWCNTs) have been provided a various unique properties: mechanical (deformation properties), electrical (high electrical conductivity) and physicochemical properties [1].

There are different methods to produce CNT: chemical vapor deposition, electric arc discharge, laser ablation, electrolysis. These methods produce different CNTs corresponding to different geometric structures. In this case, the diameters and correspondingly the lengths of the CNTs are significantly different from each other [2].

The multiple molecules can be attached to the carboxyl-functionalized MWCNTs (MWCNT-COOH) by strong covalent, hydrogen bonds or π-π stacking interactions for construction a new nano-platforms [3,4]. As example, single-walled carbon nanotubes functionalized with a carboxyl group sensor are shown sensitivity to CO gas [5].

Gadolinium – containing carbon nanomaterials are a new class of contrast agent for magnetic resonance imaging, medical and biological applications [6-8].

Thermal gravimetric analysis (TGA) and differential scanning calorimetry are considered as powerful methods for investigation and development of carbon-based nanocomposites applications [9]. Through TGA analysis studies, MWCNTs show higher air stability than MWNTs, diamond, graphite and annealed diamond produced in the high temperature range (2200 to 2800 °C). This treatment removed different types of defects [10]. Recent advances in thermal analysis of carbon nanocomposites were summarized in [11].

In addition, optimizing the effectiveness of these samples requires understanding the mechanisms of CNTs decomposition over a certain period, especially under the influence of heat [12].

In our previous studies [13-18], the synthesis of carbon nanotubes, their functionalization, doping, appropriate characteristics of their morphology, structure and photoelectric properties were studied.

The objective of this work is the comparative analysis of TGA and DSC data at 10 and 15% for different concentrations of Gd element addition in Gd-MWCNTs nanocomposites.

I. Experimental details

Sample preparation.

The multi-walled carbon nanotubes were obtained by the electric arc discharge method.

Carbon nanotubes were initially obtained by arc discharge method and then functionalized [13]. Gadolinium-doped multi-walled carbon nanotubes (Gd-MWCNTs) were obtained using a hydrothermal approach, schematically presented in Figure 1, as described in our previous research work [14]. All chemicals for synthesis were purchased from Sigma-Aldrich, USA and used as received.

Material characterization.

Hitachi HT 7700 (Japan) TEM microscopy at room temperature was used for structural investigation of Gd-MWCNT. The operating parameters of the research equipment includes: resolution equals 0.204 nm for 100 kV, magnification range 200x - 600,000x, and an accelerator voltage range 40-120 kV. Thermogravimetric analysis (TGA) was successfully performed using a NETZSCH STA 409 PC/PG setup.

II. Results and discussion

2.1. TEM

The morphology features, and Gd dopant distribution for Gd-MWCNT nanocomposite were investigated using the TEM technique for two magnifications x10.0k (1.0 µm), x120.0k (100 nm) with accelerating voltage equals 120.0 kV.

TEM images for carboxyl group-functionalized carbon nanotubes (FCNTs) were investigated in our previous work [17]. It has been confirmed that the addition of certain acids to the side wall or tip of MWCNTs by introducing a carboxylic functional group (-COOH) during chemical reactions significantly increased the solubility of MWCNTs [17].

In current research TEM was employed to get an insight into the surface morphology of the Gd-decorated/doped MWCNT nanocomposites. The tubular morphology, as well as the close to smooth and homogeneous surface was verified for Gd doped MWCNTs (same trend with FCNT).

Figure 2 and 3 shows the TEM image of prepared materials at low and high magnification. The structural features of 10% and 15 % Gd doped MWCNTs are shown in Figure 2 and 3, respectively. The TEM images for Gd-MWCNTs show that pipe wall is smooth.

Furthermore, the Gd nanoparticle dopant in bought nanocomposites are nearly spherical in shape and distributed onto the surface of MWCNT or zipped the edges of MWCNT. Minorly, aggregates are also seen. This kind structural compatibility between MWCNT and Gd dopant opens various uses specifically in catalytic sensors and heath care area (as example in bioimaging techniques).

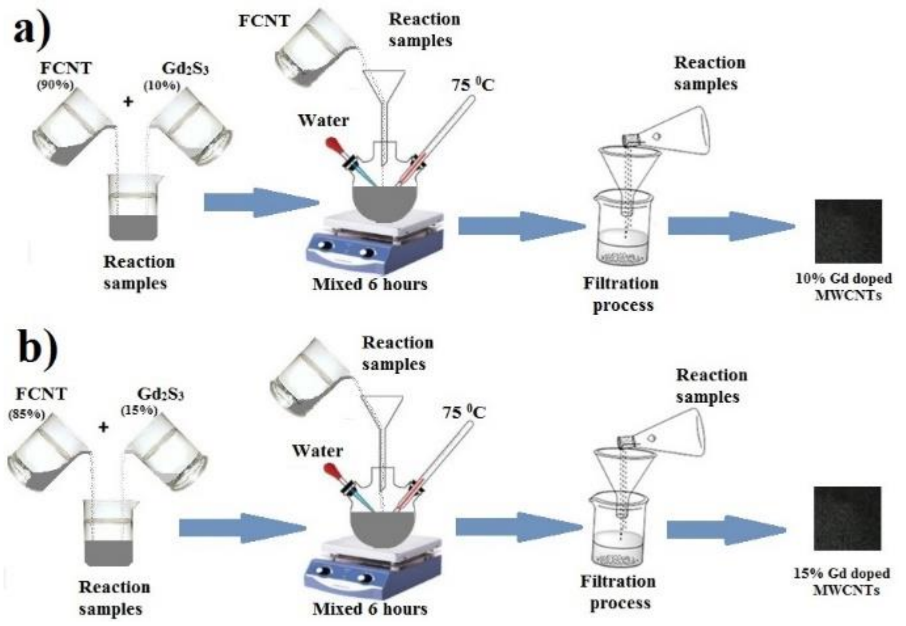
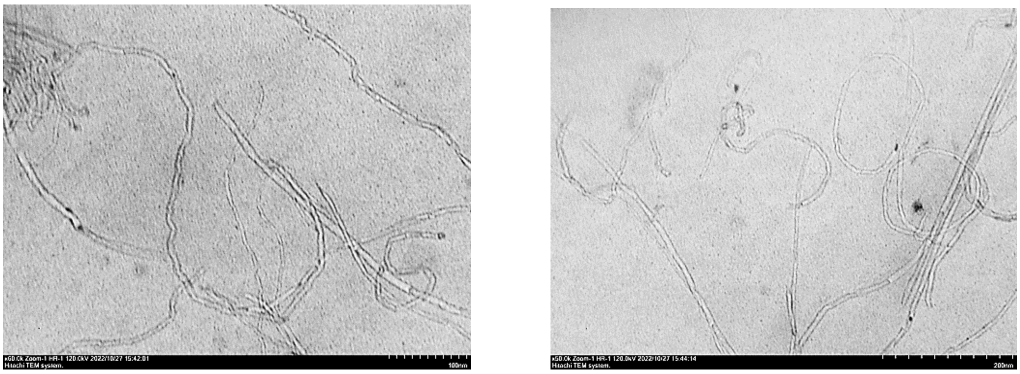
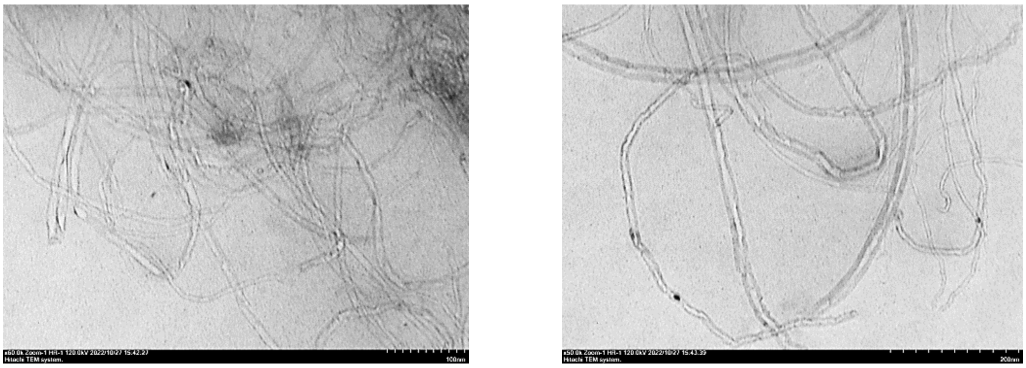


Fig.1. Schema of Gd doping process of MWCNT with different concentration of Gd: a) 10% and b) 15%, respectively.



a) b)

Fig.2. TEM images of synthesized 10 % Gd -MWCNTs (a) at low and (b) at high resolution.



a) b)

Fig.3. TEM images of synthesized 50 % Gd -MWCNTs (a) at low and (b) at high resolution.

2.2. TGA and specific heat capacity analysis

Thermogravimetric analyses were performed in the air atmosphere to see the nature and behavior of these distinctive structure in the Gd-MWCNT.

The influence of COOH- functional group modification on thermal properties MWCNTs (FCNT) was identified by TGA in our previous work [17].

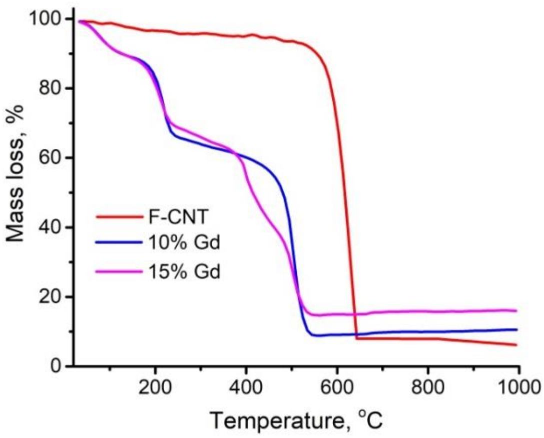


Fig. 4. TGA curves of functionalized CNTs, 10% gadolinium doped CNTs, and 15% gadolinium doped CNTs.

The TGA weight loss curves of MWCNTs with COOH- functional group (FCNT) and Gd-MWCNT are shown in Fig. 4. Thermogravimetric data of COOH functionalized was added for comparison with Gd-MWCNT to provide more detailed information about the thermal stability and surface functionalization the investigated carbon nanomaterials.

The first step (25-190°C) of ~12% mass loss belongs to the evaporation of physically adsorbed water, and it was seen in all Gd-doped CNT samples. A second degradation step (200-340 °C) with mass losses of ~27% for 10% Gd, ~25% for 15% Gd shows the decomposition of $Gd(OH)_3$ to the GdOOH intermediate product before transforming into the final product of Gd_2O3. Transformation of GdOOH into Gd_2O_3 is observed between 400 and 600 °C together with the degradation of CNT. The clear degradation of GdOOH into the final oxide product can be detected in the temperature interval of 340-490 °C in the 15% Gd-doped CNT sample. Based on TGA experiments, it is suggested that during the Gd-doped CNT synthesis reaction, gadolinium was transformed into oxide or hydroxide forms and pure Gd doping on the CNT surface was not achieved due to conducting the reaction in the presence of air instead of inert gas.

The multistep mass loss also can be associated with samples decompositions.

DSC data were used for calculation of heat capacity parameter temperature dependencies feature. The heat capacity parameters were calculated using the same approach as in [17] for constant pressure. The calculations were performed using a FORTRAN script.

As shown in Figure 5, the temperature dependences the specific heat capacities (Cp = Cp(T)) for 10% Gd-MWCNTs and 15% Gd-MWCNTs nanocomposites at constant pressure has same trend but different values.

The Cp parameter of the specific heat capacities of Gd-MWCNTs samples gradually changes with the temperature change, that is, increases, for all the studied materials. The trend of Cp parameter agreed with literature data [19-20]. The difference in Cp for different Gd dopant concentration of MWCNTs can be associated with different defect surface conditions.

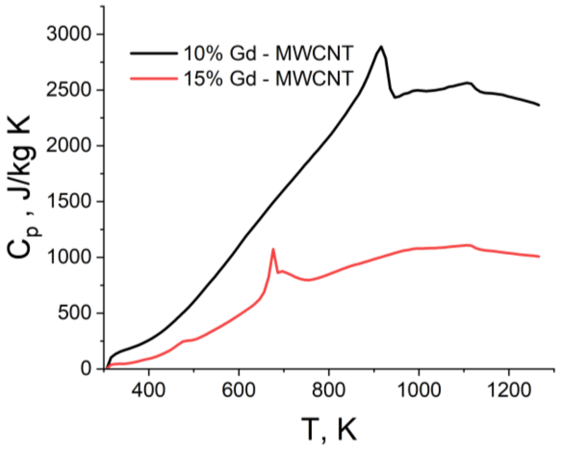


Fig. 5. Temperature dependencies of specific heat capacity parameters for 10 % Gd - MWCNT and 15% Gd-MWCNT.

It is shown in Table 1 that FCNTs samples were summarized with maximum values of specific heat capacities accordingly.

Table 1.

Data on specific heat capacities are given in comparison with FCNT.

Sample	C_p, J/kg K	
	T (K)	C_p
FCNT	916.3 [17]	1588.5 [17]
10%Gd - MWCNTs	916.290	2888.15
15%Gd - MWCNTs	1106.290	1108

Conclusion

The work represents the synthesis and thermal properties characterization of gadolinium doped MWCNT with 10 and 15 % of dopant, respectively.

The microstructure of were studied using TEM techniques. By studying Gd-MWCNTs the smooth as well and homogeneous surface morphology were observed which affected on the properties of carbon nanotubes. The distribution and location of Gd dopant on MWCNTs surfaces were confirmed.

The thermal properties for synthesized Gd-MWCNTs (with 10% and 15% dopant) were confirmed by TGA measurements. Multistep mass loss associated with material degradation and Gd-intermediate product decompositions.

During the study of DSC data, the corresponding values of specific heat capacities of Gd-MWCNTs were calculated. The specific heat capacities Cp of the investigated samples has the same dynamics. Was found that, maxima specific heat capacity for 10% Gd-doped MCNTs equals Cp = 2.88815 kJ/kg·K (T = 916,290 K) and for 15% Gd-doped MCNTs equals Cp = 1.10801 kJ/kg·K (T =1106,290 K), respectively.

***Abaszade R.G.* –** Associate Professor, PhD;
Aliyev E.M. – Postdoctoral Research Fellow, Ph.D;
Zapukhlyak R.I. – PhD, Senior Researcher;
***Mammadov A.G.* –**Doctor of technical sciences, professor;
***Khanmammadova E.A.* –** Researcher;
***Aliyev F.G.* –**Doctor of technical sciences, professor;
***Guliyev A.A.* –** Associate Professor, PhD;
***Budak H.F.* –** Researcher;
***Kasapoglu A.E.* –** Researcher;
Margitych T.O. – Researcher, PhD;
Singh A. – Researcher, PhD;
Arya S. – Associate Professor, PhD;
***Gür E.* –** Professor, PhD;
Stetsenko M.O. – Postdoctoral Research Fellow, PhD.

[1] Hira Ijaz, Asif Mahmood, Mohamed M. Abdel-Daim, Rai Muhammad Sarfraz, Muhammad Zaman, Nadiah Zafar, Sultan Alshehery, Mounir M. Salem-Bekhit, Mohammed Azam Ali, Lienda Bashier Eltayeb, Yacine Benguerba, *Review on carbon nanotubes (CNTs) and their chemical and physical characteristics, with particular emphasis on potential applications in biomedicine*, Inorganic Chemistry Communications, 155, 111020 (2023); https://doi.org/10.1016/j.inoche.2023.111020.

[2] A. Anvari, *The Influence of CNT Structural Parameters on the Properties of CNT and CNT-Reinforced Epoxy*, International Journal of Aerospace Engineering, Article ID 4873426 (2020); https://doi.org/10.1155/2020/4873426.

[3] M. Hassani, A. Tahghighi, M. Rohani, et al. *Robust antibacterial activity of functionalized carbon nanotube-levofloxacine conjugate based on in vitro and in vivo studies*. Sci.Rep. 12:10064 (2022); https://doi.org/10.1038/s41598-022-14206-w.

[4] M. Stetsenko, T. Margitych, S. Kryvyi, L. Maksimenko, A. Hassan, S. Filonenko, B. Li, J. Qu, E. Scheer, S. Snegir, *Nanoparticle Self-Aggregation on Surface with 1,6-Hexanedithiol Functionalization. Nanomaterials* 10, 512 (2020); https://doi.org/10.3390/nano10030512.

[5] D. Fu, H. Lim, Y. Shi, X. Dong, S. G. Mhaisalkar, Y. Chen, Sh. Moochhala, L.Li, *Differentiation of gas molecules using flexible and all-carbon nanotube devices*, Journal of Physical Chemistry C. 112(3), 650 (2008); https://doi.org/10.1021/jp710362r.

[6] Rodríguez-Galván A, Rivera M, García-López P, Medina LA, Basiuk VA. *Gadolinium-containing carbon nanomaterials for magnetic resonance imaging: Trends and challenges.* J Cell Mol Med., 24(7), 3779 (2020), https://doi.org/10.1111/jcmm.15065.
[7] F. Du, L. Zhang, L. Zhang, M. Zhang, A. Gong, Y. Tan, S. Zou, Engineered gadolinium-doped carbon dots formagnetic resonance imaging-guided radiotherapy of tumors, Biomaterials, 121, 109 (2017); https://doi.org/10.1016/j.biomaterials.2016.07.008.
[8] Y. Hwang, S. H. Park, J. W. Lee, *Applications of functionalized carbon nanotubes for the therapy and diagnosisof cancer*, Polymers, 9(1), 13 (2017); https://doi.org/10.3390/polym9010013.
[9] A. Vignes, O. Dufauda, L. Perrina, D. Thomas, J. Bouillard, A. Janès, C. Vallières, *Thermal ignition and self-heating of carbon nanotubes: From thermokinetic study to process safety*, Chemical Engineering Science 64, 4210 (2009); https://doi.org/10.1016/j.ces.2009.06.072.
[10] D. Bom, R. Andrews, D. Jacques, J. Anthony, B. Chen, M. S. Meier, J. P. Selegue, *Thermogravimetric Analysis of the Oxidation of Multiwalled Carbon Nanotubes: Evidence for the Role of Defect Sites in Carbon Nanotube Chemistry*, Nano Lett. 2:615 (2002); https://doi.org/10.1021/nl020297u.
[11] A.G. Bannov, M.V. Popov, P.B. Kurmashov, *Thermal analysis of carbon nanomaterials: advantages and problems of interpretation*, Journal of Thermal Analysis and Calorimetry 142, 349 (2020); https://doi.org/10.1007/s10973-020-09647-2.
[12] M.A.Arshad, *Thermo-oxidative decomposition of multi-walled carbon nanotubes: Kinetics and Thermodynamics*, Fullerenes, nanotubes and carbon nanostruktures, 28, 23 (2020); https://doi.org/10.1080/1536383X.2020.1775591.
[13] R.G. Abaszade, O.A. Kapush, S.A. Mamedova, A.M. Nabiyev, S.Z. Melikova, S.I. Budzulyak, *Gadolinium doping influence on the properties of carbon nanotubes*, Physics and Chemistry of Solid State, 21(3), 404 (2020); https://doi.org/10.15330/pcss.21.3.404-408.
[14] R.G. Abaszade, M.B. Babanli, V.O. Kotsyubynsky, A.G. Mammadov, E. Gür, O.A. Kapush, M.O.Stetsenko, R.I.Zapukhlyak, *Influence of gadolinium doping on structural properties of carbon nanotube*, Physics and Chemistry of Solid State, 24(1), 153 (2023); https://doi.org/10.15330/pcss.24.1.153-158.
[15] A.G. Mammadov, R.G. Abaszade, V.O. Kotsyubynsky, E.Y. Gur, I.Y. Bayramov, E.A. Khanmamadova, O.A. Kapush, *Photoconductivity of carbon nanotubes*, Technical and Physical Problems of Engineering, 14(3), 155 (2022).
[16] A.G. Mammadov, R.G. Abaszade, M.B. Babanli, V.O. Kotsyubynsky, E. Gur, B.D. Soltabayev, T.O. Margitych M.O. Stetsenko, *Photoconductivity of gadolinium-doped carbon nanotubes*, Technical and Physical Problems of Engineering, 15, 56(3), 53 (2023).
[17] R.G. Abaszade, E.M. Aliyev, M.B. Babanli, V.O. Kotsyubynsky, R.I. Zapukhlyak, A.G. Mammadov, H.F. Budak, A.E. Kasapoglu, E. Gür, T.O. Margitych, M.O. Stetsenko, *Investigation of thermal properties of carbon nanotubes and carboxyl group-functionalized carbon nanotube*, Physics and Chemistry of Solid State, 24(3), 530 (2023); https://doi.org/10.15330/pcss.24.3.530-535.
[18] R.G. Abaszade, O.A. Kapush, A.M. Nabiyev, *Properties carbon nanotubes doped with gadolinium*, Journal of optoelectronics and biomedical materials, 12(3), 61 (2020); https://www.chalcogen.ro/61_AbaszadeRG.pdf
[19] N.R Pradhan, H Duan, J. Liang, G.S. Iannacchione, *The specific heat and effective thermal conductivity of composites containing single-wall and multi-wall carbon nanotubes*, Nanotechnology, 20, 245705 (2009); https://doi.org/10.1088/0957-4484/20/24/245705.
[20] K.S. Patil, G.R. Gupta, *Thermal investigations of multiwall carbon nanotubes*, *International Journal of Management, Technology And Engineering* Volume IX, Issue I, (2019); https://ijamtes.org/gallery/187-jan19.pdf.

Р.Г. Абасзаде[1,2], Е.М. Алієв[3], А.Г. Маммадов[1], Е.А. Ханмамадова[1], А.А. Гулієв[1], Ф.Г. Алієв[2], Р.І. Запухляк[4], Х.Ф. Будак[5], А.Е. Касапоглу[5], Т.О. Маргітич[6], А. Сінх[7], С. Арія[7], Е. Гюр[8], М.О. Стеценко[9]

Дослідження термічних властивостей вуглецевих нанотрубок допованих гадолінієм

[1]*Азербайджанський державний університет нафти і промисловості, Баку, Азербайджан,* abaszada@gmail.com,
[2]*Азербайджанський університет архітектури і будівництва, Баку, Азербайджан,* abaszada@gmail.com,
[3]*Університет Бірмінгему, Еджбастон, Велика Британія,* e.aliyev@bham.ac.uk,
[4]*Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна,* kotsuybynsky@gmail.com,
[5]*Офіс Центру досліджень і застосувань високих технологій Східної Анатолії, Ерзурум, Туреччина,* hfeyzi.budak@atauni.edu.tr, aemre.kasapoglu@atauni.edu.tr,
[6]*Київський інститут ядерних досліджень, НАН України, Київ, Україна,* margtanya@gmail.com,
[7]*Фізичний факультет, Університет Джамму, Джамму, Індія,* snp09arya@gmail.com,
[8]*Університет Ескішехір Османгазі, Ескішехір, Туреччина,* emregur@ogu.edu.tr,
[9] *Ключова лабораторія оптоелектронних пристроїв і систем, Коледж фізики та оптоелектронної інженерії, Шеньчженьський університет, Шеньчжень, КНР,* stetsenkomax@gmail.com

Досліджено характеристики теплових властивостей багатостінних вуглецевих нанотрубок (МВНТ), легованих 10% та 15% Gd. Відповідні характеристики дослідження були досліджені за допомогою методів TGA/DSC та TEM. Проаналізовано характеристики втрати маси для синтезованих нанокомпозитних вуглецевих наноматеріалів. Помічено, що питома теплоємність досліджуваних зразків зростала пропорційно з ростом температури.

Ключові слова: Гадоліній, метод дугового розряду, MWCNT, TEM, TGA, питома теплоємність.