VII EMR-PL Forum

25-28 June 2024 University of Zielona Góra

Under the honorary patronage

Prof. dr hab. Wojciech Strzyżewski, the Rector UZ

UNIVERSITY
OF ZIELONA GÓRA

PG EMR

Editor: Ryszard Piotrowski

CONTENTS

COMMITTEES

SCIENTIFIC COMMITTEE

Prof. dr hab. Czesław Rudowicz, Adam Mickiewicz University, Poznań

Prof. dr hab. Zbigniew Sojka, Jagiellonian University in Kraków

Prof. dr hab. Alina Bieńko, University of Wrocław

Prof. dr hab. Niko Guskos, West Pomeranian University of Technology, Szczecin

Prof. dr hab. Martyna Elas, Jagiellonian University in Kraków

Prof. dr hab. Maria Augustyniak-Jablokow, Institute of Molecular Physics of the Polish Academy of Sciences, Poznań

Prof. dr hab. Waldemar Bednarski, Institute of Molecular Physics of the Polish Academy of Sciences, Poznań

Prof. dr hab. Izabela Sadowska-Bartosz, University of Rzeszów, College of Natural Science

Prof. dr hab. Grzegorz Bartosz, University of Rzeszów, College of Natural Science

Prof. dr hab. Mirosław Dudek, University of Zielona Góra

Prof. dr hab. Wojciech Kempiński, Institute of Molecular Physics of the Polish Academy of Sciences, Poznań

Dr hab. Piotr Pietrzyk, Jagiellonian University in Kraków

Dr hab. Bohdan Padlyak, University of Zielona Góra

Dr hab. Ireneusz Stefaniuk, University of Rzeszów

PROGRAMME COMMITTEE

Dr hab. Piotr Pietrzyk, Chairman of the Polish EMR Group, Jagiellonian University in Kraków

Prof. dr hab. Czesław Rudowicz, Founding Chairman of the Polish EMR Group, Adam Mickiewicz University, Poznań

Dr hab. Bohdan Padlyak, 1st Vice-Chairman of the Polish EMR Group, Chair of Local Organizing Committee, University of Zielona Góra

Dr hab. Ireneusz Stefaniuk, 2nd Vice-Chairman of the Polish EMR Group, University of Rzeszów

Prof. dr hab. Alina Bieńko, Wrocław University

Prof. dr hab. Maria Augustyniak-Jablokow, Institute of Molecular Physics, Polish Academy of Sciences, Poznań

LOCAL ORGANIZING COMMITTEE

Dr hab. Bohdan Padlyak - Chairman of the LOC, Prof. of the University of Zielona Góra

Dr hab. Piotr Pietrzyk - Vice-Chaiman of the LOC, Prof. of the Jagiellonian University in Kraków, Chairman of the Polish EMR

Dr hab. Maria Przybylska - Vice-Chairwoman of the LOC, Prof. of the University of Zielona Góra

Prof. dr hab. Czesław Rudowicz - Honorary Chairman of the LOC, Adam Mickiewicz University, Poznań

Dr hab. Ireneusz Stefaniuk - Member of the LOC, Website Moderator, Prof. of the University of Rzeszów

Dr Kamila Sobańska - Secretary of the LOC, Jagiellonian University in Kraków

Prof. dr. hab. Mirosław Dudek - Member of the LOC, University of Zielona Góra

Dr Adam Drzewiecki - Member of the LOC, Technical support, University of Zielona Góra

Mgr Ryszard Piotrowski - Member of the LOC, Webmaster, University of Zielona Góra

CONFERENCE PROGRAMME

25.06.2024, Tuesday **(Venue:** 4a Prof. Z. Szafrana Street, Building A-29**)**	
12:00 – 17:00	**REGISTRATION (1st floor, Hall near Aula 106)**
17:00 – 17:30	**OPENING CEREMONY (1st floor, Aula 106)** Chairwoman: **Dr hab. Maria Przybylska, Prof. UZ** (Zielona Góra), Chairwoman of the Local Organizing Committee (LOC) of the VII Forum EMR-PL; Welcome address: **Dr hab. Piotr Pietrzyk, Prof. UJ** (Kraków), Chairman of the Polish Electron Magnetic Resonance (EMR–PL) Group; **Prof. dr hab. Wojciech Strzyżewski** (Zielona Góra), the Rector UZ, Honorary Patronage of the VII Forum EMR-PL; **Prof. dr hab. Andrzej Drzewiński** (Zielona Góra), Dean of the Faculty of Physics and Astronomy UZ; **Dr hab. Bohdan Padlyak, Prof. UZ** (Zielona Góra), Chairman of the Local Organizing Committee (LOC) of the VII Forum EMR-PL **COMMEMORATIVE GROUP PHOTOS**
17:30 – 19:30	**WELCOME RECEPTION (ground floor, cafeteria “Kuchnia u Macieja”)**
26.06.2024, Wednesday **(Venue:** 4a Szafrana Str. Building A-29, 1st floor, Aula 106**)**	
8:30 – 9:00	**REGISTRATION (1st floor, Hall near Aula 106)**
1st Oral session, Chairman: Dr hab. Maciej Witwicki, Prof. UWr	
9:00 – 9:40	C. Rudowicz, L. Mollabashi, S. Jalali-Asadabadi, M. Acikgoz, Z. Ghasemi-Dorcheh, R. Ebrahimi-Jaberi, M. Jalali-Asadabad, S. Rahimi, F. Jalali-Asadabadi ***Interplay between spin Hamiltonian and crystal field Hamiltonian: DFT/ab initio and semiempirical modelling for Gd_{3+} ions in $PbTiO^3$ and Tm_{3+} ions in $LiTmF_4$*** **(Plenary Lecture 1)**
9:40 – 10:10	Maciej Marć , Wiktor W. Wolak, Andrzej Drzewiński, Stepan Mudry, Ihor Shtablavyi, Miroslaw R. Dudek ***Kittel's theory of ferromagnetic resonance for thin, flexible films with embedded magnetic nanostructures*** **(O-1)**
10:10 – 10:40	Jacek Sawka, Alina Bieńko, Anna Świtlcka, Roman Boča, Andrew Ozarowski ***The impact of linker ligands on the structure dimensionality, magnetic anisotropy and slow relaxation processes of six-coordinate Ni(II) complexes*** **(O-2)**
10:40 – 11:20	Bohdan Padlyak, Ihor Kindrat, Adam Drzewiecki, Ireneusz Stefaniuk ***EPR spectroscopy of the $Li_2B_4O_7$ glasses co-doped with transition (Cu, Mn) and rare-earth (Eu, Sm) elements (review)*** **(Plenary Lecture 2)**
11:20 – 11:50	**COFFEE BREAK (ground floor, cafeteria “Kuchnia u Macieja”)**

2nd Oral session, Chairman: Dr hab. Piotr Pietrzyk, Prof. UJ	
11:50 – 12:30	Maria Augustyniak-Jabłokow, Roman Strzelczyk, Ryhor Fedaruk ***Methodology of EMR Investigations of the Graphene Related Carbon Materials* (Plenary Lecture 3)**
12:30 – 13:00	Krzysztof Kruczała, Radim Beranek, Szymon Wierzbicki ***Study of Catalytic Systems by Electron Paramagnetic Resonance Spectroscopy* (O-3)**
13:00 – 13:30	**Maciej Witwicki** ***Metal Cation Radical Complexes: From Environmental Pollutants to Functional Materials* (O-4)**
13:30 – 15:00	**LUNCH (ground floor, cafeteria “Kuchnia u Macieja”)**
3rd Oral session, Chairman: Dr hab. Ireneusz Stefaniuk, Prof. UR	
15:00 – 15:40	Dana Dvoranová, Zuzana Dyrčíková ***The cw-Electron Paramagnetic Resonance Spectroscopy in Heterogeneous Photocatalysis* (Plenary Lecture 4)**
15:40 – 16:10	Aneta Krasowska, Paweł Rejmak, Piotr Pietrzyk ***From dioxygen to superoxide – EPR study of paramagnetic Zn^{2+}-$O_2^{\bullet-}$ species in ZSM-5 zeolite and periodic DFT modelling* (O-5)**
16:10 – 16:40	Kamila Sobańska, Piotr Pietrzyk ***Identification of reactive oxygen species generated by the interaction of transition metal oxides and H_2O_2* (O-6)**
16:40 – 17:10	**General Meeting of the Polish EMR Group**
17:10 – 17:40	**COFFEE BREAK (ground floor, cafeteria “Kuchnia u Macieja”)**
17:40 – 19:00	**POSTER SESSION, Chairman: Prof. dr hab. Mirosław Dudek** (1st floor, Hall near Aula 106) **(P-1) Zuzana Dyrčíková**, Miriama Malček Šimunková, Dana Dvoranová ***Photoinduced processes on modified titanium dioxide photocatalysts studied by indirect cw-EPR techniques*** **(P-2) Zuzanna Didjurgeit, Iga Sienkiewicz**, Adrianna Kędziora, Beata Kucharska, Bernadeta Dobosz ***Herbs with antioxidant and photosensitizing properties*** **(P-3) Vasyl Tataryn**, Bohdan Padlyak, Oleksiy Tataryn ***System of digital scanning of the magnetic field for radiospectrometers of the “RADIOPAN” company (Poznań, Poland)*** **(P-4)** Kacper Kut, Bogumił Cieniek, Ireneusz Stefaniuk, Grzegorz Bartosz, **Izabela Sadowska-Bartosz** ***Effect of low concentrations of nitroxides on SH-SY5Y cells transfected with the Tau protein*** **(P-5) Łukasz Dubiel**, Antoni Żywczak, Andrzej Wal, Ireneusz Stefaniuk ***Electron magnetic resonance of Co-doped $BaTiO_3$ ceramics at helium temperatures***

	(P-6) Bogumił Cieniek, Ireneusz Stefaniuk, Magdalena Kulpa-Greszta, Anna Tomaszewska, Robert Pązik ***EMR study of spinel multi-shell $CoFe_2O_4$ nanoferrites*** **(P-7) Ihor Kindrat**, Bohdan Padlyak, Adam Drzewiecki, Volodymyr Adamiv, Ihor Teslyuk, Bogumił Cieniek, Ireneusz Stefaniuk ***EPR and optical spectroscopy of lithium tetraborate glasses doped with Tb and co-doped with Tb and Ag*** **(P-8) Iwona Rogalska**, Bogumił Cieniek, **Ireneusz Stefaniuk**, Marta Ruszała, Jakub Grendysa, Anna Juś ***Properties of Cd1-xMnxTe as a room temperature semiconductor radiation detector*** **(P-9) Danuta Piwowarska**, Niko Guskos, Konstantinos Aidinis, Ewelina Kusiak-Nejman, Agnieszka Wanag, Antoni W. Morawski ***Temperature dependence of EPR spectra in titanium dioxide modified with (3-aminopropyl) triethoxysilane (APTES)*** **(P-10)** T. Jasiński, M. Drąg, **M. Kuzma** ***Spin qubit pairs in DNA Hairpins – EPR methods of study***
27.06.2024, Thursday **(Venue:** 4a Szafrana Str. Building A-29, 1st floor, Aula 106**)**	
4th Oral session, Chairman: Prof. dr hab. Czeslaw Rudowicz, UAM	
9:00 – 9:20	**Zbigniew Sojka** *In Memory of Professor Krystyna Dyrek* **(Invited Lecture)**
9:20 – 10:00	**Zbigniew Sojka** *EPR and DFT Investigations into Reactive Oxygen Species Trapped on Surfaces and in Cages of Catalytic Relevance* **(Plenary Lecture 5)**
10:00 – 10:30	**Krystian Mokrzyński**, Andrzej Żądło, Grzegorz Szewczyk, Michał Sarna, Theodore G. Camenisch, Shosuke Ito, Kazumasa Wakamatsu, Tadeusz Sarna *The effect of oxidative degradation of Dopa-melanin on its basic physicochemical properties and photoreactivity* **(O-7)**
10:30 – 11:00	**Katarzyna Zawada**, Katerina Makarova, Małgorzata Korzeniowska nee Wiweger *Benchtop X-band EPR for in vivo studies of zebrafish - melanin radicals and nitroxyl spin probes* **(O-8)**
11:00 – 11:30	**COFFEE BREAK (ground floor, cafeteria “Kuchnia u Macieja”)**
5th Oral session, Chairman: Prof. Dr hab. Zbigniew Sojka, UJ	
11:30 – 12:10	**Alina Bieńko** *Towards "better" molecular magnets. Correlation of structure and magnetic anisotropy* **(Plenary Lecture 6)**
12:10 – 12:40	**Marian Kuzma**, M. Bester, B. Cieniek, V. Popowich, I. Stefaniuk *Two-dimensional magnetism in a self-intercalated transition metal dichalcogenides* **(O-9)**

12:40 – 13:30	**Free time before Conference excursion and Gala dinner**
13:30 – 15:00	**LUNCH (ground floor, cafeteria “Kuchnia u Macieja”)**
15:00 – 18:00	**Bus and boat excursion to the “Winny Dworek” including tasting of local wines and cheeses**
18:00 – 20:00	**Conference Gala Dinner in the restaurant at "Winny Dworek"**
20:00 – 21:00	**Departure to Zielona Góra**

28.06.2024, Friday
(Venue: 4a Szafrana Str. Building A-29, 1st floor, Aula 106**)**

6th Oral session, Chairman: Dr hab. Bohdan Padlyak, Prof. UZ

10:00 – 10:30	<u>Bernadeta Dobosz</u> ***Application of ESR spectroscopy in nanomedicine (O-10)***
10:30 – 11:00	<u>Ireneusz Stefaniuk</u>, Bogumił Cieniek, Agata Ćwik, Katarzyna Kluska, Idalia Kasprzyk ***EPR case study - tracking long-lived free radicals in dandelion caused by air pollution*** **(O-11)**
11:00 – 11:30	**COFFEE BREAK (ground floor, cafeteria “Kuchnia u Macieja”)**
11:30 – 12:00	**CLOSING REMARKS AND CONCLUSION OF THE FORUM**
12:00 – 13:30	**LUNCH (ground floor, cafeteria “Kuchnia u Macieja”)**

Categories & Duration of the presentations

1. **Plenary**: 40min (35 min + 5 min for discussion);
2. **Invited**: 40min (35 min + 5 min for discussion);
3. **Oral**: 30 min (25 min + 5 min for discussion).

NOTES:

* **Session Chairman are kindly requested to inform each presenter**:

– about 10 min before the end of presentation that there are “***10 min left including discussion***”;

– about 5 min before the end of presentation that “***the remaining time should be devoted for discussion***”.

*** Presenters are kindly requested to upload the file with your presentation into the conference computer before the start of a given session, unless you intend to use your own notebook.**

Interplay between spin Hamiltonian and crystal field Hamiltonian: DFT/ab initio and semiempirical modelling for Gd^{3+} ions in $PbTiO_3$ and Tm^{3+} ions in $LiTmF_4$

C. Rudowicz[a], L. Mollabashi[b], S. Jalali-Asadabadi[b], M. Acikgoz[c],
Z. Ghasemi-Dorcheh[b], R. Ebrahimi-Jaberi[b], M. Jalali-Asadabad[b], S. Rahimi[a], F. Jalali-Asadabadi [b,d]

[a] *Faculty of Chemistry, A. Mickiewicz University (AMU), Poznań, Poland*
[b] *Department of Physics, Faculty of Physics, University of Isfahan (UI), Isfahan, Iran*
[c] *Department of Science, State University of New York (SUNY) Maritime College, USA*
[d] *Physics Department, Faculty of Science, Razi University, Kermanshah, Iran*

saeid.jalali.asadabadi@gmail.com; czeslaw.rudowicz@amu.edu.pl

Key words: spin Hamiltonian theory; crystal field theory; modelling of SH and CF parameters; Gd^{3+} doped in $PbTiO_3$; Tm^{3+} ions in $LiTmF_4$; magnetization and susceptibility.

Part (A) recaps two approaches: the density functional theory (DFT)/ab initio and superposition model (SPM) analysis, for modelling of spin Hamiltonian (SH), including the zero-field splitting parameters (ZFSPs), and the crystal field Hamiltonian (CFH) parameters (CFPs).

Part B1 presents our studies[1] of **Gd^{3+} ions in $PbTiO_3$**: (i) structural changes in Gd^{3+}-doped $PbTiO_3$ that are crucial for potential applications in photonics; (ii) DFT) optimization of structural data, which then serve as input for superposition model (SPM) analysis; (iii) computation of the formation energies of Gd^{3+}: $PbTiO_3$ with and without O-vacancy to determine the stable composition; (iv) various structural models of Gd^{3+}:$PbTiO_3$ used as input for SPM/ZFP modelling to analyze variations of ZFSPs from 5 to 780 K. The results were fine-tuned by matching with available experimental EMR data for Gd^{3+} probes in $PbTiO_3$ nanoparticles. The combined DFT+SPM modeling provides reliable description of experimental data and confirms the plausibility of Gd^{3+} entering Pb^{2+} sites.

Part B2 presents our studies[2] of **Tm^{3+} ions in $LiTmF_4$:** (i) magnetic properties of $LiTmF_4$, which promises applications in, e.g. MRI and spintronics; (ii) DFT/ab initio and SPM modeling of CFPs and the Zeeman *g*-factors; (iii) distinction between the complete (7 independent CFPs) and reduced (6 independent CFPs) approaches; (iv) computing the conserved CFP quantities predicted by the Noether theorem; (v) analysis of CF multiplet splitting in magnetic ***B***-field as well as computing ionic magnetic moment and temperature dependencies of magnetic susceptibility. Our findings agree with experimental data thus indicating efficacy of the combined DFT+CFT+Δ/SPM+CFT modeling.

Part (C) elucidates interplay between SH and CFH: (i) symmetry aspects: ascend of site symmetry of Gd^{3+} in $PbTiO_3$ from tetragonal type I to cubic at higher temperatures *verus* tetragonal type II S_4 site symmetry of Tm^{3+} in $LiTmF_4$; (ii) origin of the SH parameters, including ZFSPs and *g*-factors; (iii) the ZFS=CF and CF=ZFS confusion regarding these notions.

Acknowledgements: Poznań Supercomputing and Networking Centre Grant #353.

---

[1] M. Açıkgöz, et al. Physical Chemistry Chemical Physics, 25 (2023) 3986–4004.

[2] L. Mollabashi, et al., submitted in March 2024 to Physical Review B.

EPR spectroscopy of the Li2B4O7 glasses co-doped with transition (Cu, Mn) and rare-earth (Eu, Sm) elements (review)

Bohdan Padlyak [a,b], Ihor Kindrat [a], Adam Drzewiecki [a], Ireneusz Stefaniuk [c]

[a] *University of Zielona Góra, Institute of Physics, 4a Szafrana Str., 65-516 Zielona Góra, Poland*
[b] *Ivan Franko National University of Lviv, Vlokh Institute of Physical Optics, 23 Dragomanov Str., 79005 Lviv, Ukraine*
[c] *University of Rzeszów, Institute of Materials Engineering, 16a Rejtana Str., 35-310 Rzeszów, Poland*

B.Padlyak@if.uz.zgora.pl; ikindrat@if.uz.zgora.pl; A.Drzewiecki@if.uz.zgora.pl; istefaniuk@ur.edu.pl

Key words: $Li_2B_4O_7$ glass; EPR; Cu^{2+} ions; Mn^{2+} ions, Sm^{3+} ions; spin-Hamiltonian parameters.

The $Li_2B_4O_7$:Cu,Eu glass containing 1.0 mol.% CuO and Eu_2O_3 impurities as well as $Li_2B_4O_7$:Mn,Sm glass containing 1.0 mol.% MnO_2 and Sm_2O_3 impurities were obtained by high temperature melting technology and detailed studied by XRD, EPR, optical absorption, and photoluminescence methods [1,2]. Parameters of the local structure (interatomic distances and coordination numbers) for studied glasses were derived from experimental XRD data analysis.

The EPR and optical absorption, emission, photoluminescence excitation show that the Cu impurity is incorporated into the $Li_2B_4O_7$ glass as Cu^{2+} ($3d^9$) and Cu^+ ($3d^{10}$) ions. The Cu^{2+} ions (electron spin $S = 1/2$) in the $Li_2B_4O_7$:Cu,Eu glass show typical EPR spectrum of axial symmetry with characteristic 4-component hyperfine structure caused by nuclei of ^{63}Cu (natural abundance – 69.17 %, nuclear spin, $I = 3/2$) and ^{65}Cu (30.83 %, $I = 3/2$) isotopes The precise spin Hamiltonian parameters ($g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$) and peak-to-peak first derivative linewidths of the hyperfine components ($\Delta H_{pp}{}^{||}$ and $\Delta H_{pp}{}^{\perp}$) for Cu^{2+} ions at T = 295 K in the $Li_2B_4O_7$:Cu,Eu glass were obtained by best fitting of the simulated EPR spectrum to the experimental spectrum.

The EPR and optical spectroscopy (absorption, luminescence excitation, emission, decay kinetics) show the presence of Mn^{2+}($3d^5$) and Mn^{3+}($3d^4$) impurity ions in the $Li_2B_4O_7$:Mn,Sm glass. The Mn^{2+} ($3d^5$) ions (electron spin $S = 5/2$) in the $Li_2B_4O_7$:Mn,Eu glass show an isotropic EPR spectrum with a characteristic 6-component hyperfine structure caused by nuclei of the ^{55}Mn isotope (natural abundance – 100 %, $I = 5/2$). Parameters of all observed EPR spectra of the Mn^{2+} centres in $Li_2B_4O_7$:Mn,Eu glass were determined at T = 295 K. By EPR spectroscopy in the studied glass were identified three types of the Mn^{2+} centres: single Mn^{2+} (1) centres in the strongly distorted sites (ratio of rhombic and axial constants, $|E/D| \leq 1/3$), single Mn^{2+} (2) centres in the sites with almost cubic symmetry ($D \cong 0$, $E \cong 0$) as well as Mn^{2+} pairs and small clusters coupled by magnetic dipolar and exchange interaction, respectively.

Acknowledgments. This work was supported by the Ministry of Education and Science of Ukraine (research project No. 0122U001833, realized in the Vlokh Institute of Physical Optics, Lviv, Ukraine).

References

[1] B.V. Padlyak, I.I. Kindrat, V.T. Adamiv, Y.O. Kulyk, I.M. Teslyuk, A. Drzewiecki, I. Stefaniuk, Mater. Res. Bull. 167 (2023) 112432.

[2] B.V. Padlyak, I.I. Kindrat, V.T. Adamiv, A. Drzewiecki, I. Stefaniuk, Mater. Res. Bull. 175 (2024) 112788.

Methodology of EMR Investigations of the Graphene-Related Carbon Materials

Maria Augustyniak-Jabłokow[a], Roman Strzelczyk[a], Ryhor Fedaruk[a]

[a] *Institute of Molecular Physics of Polish Academy of Sciences, 17 Smoluchowski Str., 60-179 Poznań, Poland*

maria.augustyniak@ifmpan.poznan.pl; roman.strzelczyk@ifmpan.poznan.pl; ryhor.fedaruk@ifmpan.poznan.pl

Key words: EMR techniques; carbon materials; sample preparation; lineshape; vacuum Rabi oscillations.

Carbon nanomaterials are of interest for new technologies and applications. Therefore their properties are intensively studied using various methods. Because many of these materials contain paramagnetic centers (PCs), electron magnetic resonance (EMR) can be an effective method for studying them. The continuous wave (CW) EMR spectra of carbon materials are usually simple and consist of one or two overlapping Lorentzian lines differing only in linewidth, with *g*-factor close to that of a free electron. These simple spectra make it difficult to extract useful information about the properties of the studied materials and sometimes even to identify PCs. Some additional difficulties are caused by electrical conductivity of these materials manifesting in the Dysonian distortion of the resonant line and decreasing a quality factor of resonator. Moreover, it was recently shown that high spin concentration of PCs with a narrow EMR line can result in distortions of the CW EMR spectrum due to a cavity quantum electrodynamics effect called a vacuum Rabi splitting. Temperature dependencies of CW spectra expand the possibilities of extracting useful information. Additional EMR techniques, such as pulsed EMR, are also needed to overcome difficulties in studying these materials. However, our experience has shown that recording CW EMR spectra of carbon materials, due to their specific properties, requires special attention. The first challenge is proper preparation of the sample, which, generally, should be small, diluted in diamagnetic media and be subjected to vacuum before measurement. These requirements result from the properties of the material and the physical phenomena accompanying magnetic resonance.

In this report, the impact of such phenomena as the skin effect, vacuum Rabi splitting, or microwave heating on the EMR spectra is discussed. As a result, a protocol for sample preparation and EMR measurements is proposed. We believe that this will provide repeatable and reliable results.

The cw-Electron Paramagnetic Resonance Spectroscopy in Heterogeneous Photocatalysis

Dana Dvoranová [a], Zuzana Dyrčíková [a]

[a] *Slovak University of Technology in Bratislava, Faculty of Chemical and Technology, Institute of Physical Chemistry and Chemical Physics, Radlinského 9, SK-812 37 Bratislava, Slovak Republic*

dana.dvoranova@stuba.sk; zuzana.dyrcikova@stuba.sk

Key words: photocatalysis; indirect EPR techniques; photoinduced electron transfer; reactive oxygen species.

The heterogeneous photocatalysis represents one of the effective methods within the Advance Oxidation processes (AOPs). The crucial role here plays hand in hand the material of photocatalyst, and harvested light. The Achilles' heel of most utilized metal oxides (titanium dioxide or zinc oxide) as photocatalysts is their absorption in the UV region, so currently the main goal is preparation of photocatalytic material active upon solar light exposure. The metals/non-metals doing/decorating or modification with other semiconductors have been proposed as promising way to improve the absorption in the visible region and charge carrier separation. Charge transfer processes upon photoexcitation of nanocrystalline photocatalysts initiate the generation of paramagnetic species and radical intermediates, the nature and quantity of which are determined not only by the photocatalyst properties, but also by the physicochemical factors affecting the light absorption by the photocatalyst, the quantity and nature of adsorbed species, desorption of products or the interface properties. Here the cw-electron paramagnetic resonance (EPR) spectroscopy is of utmost importance for their detection. The EPR measurements at low temperatures (*e.g.,* 100 K) have potential to detect and identify the paramagnetic centers/defects in studied samples formed *via* synthetic/postsynthetic treatment and trapped charge carriers (electron/hole) produced by photoexcitation of photocatalyst. Although EPR provides direct detection of free radicals, in photocatalytic investigations utilization of indirect techniques, such spin trapping, spin scavenging, oxidation of sterically hindered amines or photoreduction, is often applied. The evaluation of the photocatalytic activity of individual metal oxide structures is based on the nature and quantity of reactive radical intermediates generated in the irradiated semiconductor dispersions obtained by *in situ* EPR spectroscopy. Proper choice of suitable experimental conditions is crucial for their successful application in heterogeneous semiconductor systems and can help to gain a comprehensive picture of the photoinduced processes undergoing upon light exposure of the photocatalyst in suspensions.

Acknowledgments. This study was financially supported by the Slovak Research and Development Agency under the contracts Nr. APVV-19-0024, Nr. APVV-21-0039 and Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0422/24).

References

[1] D. Dvoranová, Z. Barbieriková, V. Brezová, Molecules, 18 (2014) 17279.

[2] Z. Barbieriková, D. Dvoranová, V. Brezová, Mat. Sci. Photocat., Elsevier, Ch. 8 (2021) 125.

[3] D. M. Tobaldi, D. Dvoranová, L. Lajaunie, et al., Mater. Today Energy, 15 (2022) 100974.

EPR and DFT Investigations into Reactive Oxygen Species Trapped on Surfaces and in Cages of Catalytic Relevance

Zbigniew Sojka

Faculty of Chemistry Jagiellonian University, ul. Gronostajowa 2, 30-387 Krakow, Poland

sojka@chemia.uj.edu.pl

Key words: EPR; DFT; oxygen activation; zeolites; oxides.

The chemistry of oxygen species at heterogeneous surfaces and interface has attracted a wide attention over the years owing to its vital relevance for thermal catalysis, photocatalysis, electrocatalysis and materials science as well for development of mimetic systems. Due to the peculiar properties associated with its triplet, $^3\Sigma^-_g$, ground state that hinders the reactivity, dioxygen molecules are usually activated on catalytic surfaces by a sequence of gradual reduction and dissociation steps $O_{2(g)} \rightarrow O_{2(a)} \rightarrow O_2^-{}_{(ads)} \rightarrow O^-{}_{(ads)} \rightarrow O_2^{2-}{}_{(ads)} \rightarrow O^{2-}{}_{(lattice)}$, where various surface reactive oxygen species (surface ROS), ranging from electron-poor (electrophilic) to electron-rich (nucleophilic), of distinctly different reactivity and proton affinity appear. Among them the paramagnetic $O_2^-{}_{(ads)}$ ($S = ½$) and $O^-{}_{(ads)}$ ($S=1/2$) species are EPR active. The catalytic role of the surface is to provide oxygen in a specific activated state, which permits a new reaction pathway of lower activation energy to take place. Many experimental and theoretical investigations have been devoted to detailed elucidation of these activation processes, starting from the early stages of O_2^- formation via an interfacial electron transfer until final incorporation of the resultant O^{2-} ion into the oxide lattice. Massive and porous oxide systems containing isolated, clustered or periodically extended transition metal ions belong to the most active materials for heterogeneous activation of dioxygen.

This paper reports on the activation of dioxygen on transition metal ions dispersed inside the nanopores of the zeolites and on transition metal oxides exemplified by metallozeolites, supported systems containing andspinels (Ni/MFI, Fe/MFI, Cu/MFI, Cu/CHA VO_2/BEA, ($MoO_x/SiAO_2$, Co_3O_4, Co-MgO). Experimental EPR investigations using isotopically enriched O-17 and O-18 dioxygen were corroborated by DFT modeling to provide a detailed molecular and phenomenological description of heterogeneous activation of dioxygen. Reversible and irreversible pathways of interfacial electron transfer activation of O_2 were identified. Molecular resolution approach was used, in turn, for an in-depth insight into the ET events. In this context charge and the spin density redistribution along the π, σ, and δ orbital channels in the course of oxygen activation by transition metal centers were analyzed be means of the extended transition state - natural orbitals for chemical valence approach (ETS-NOCV). Congruent and incongruent charge and spin density flows were identified to contribute jointly to the activation of the attached dioxygen species. Their individual energetic relevance was quantified, which allowed for explaining the oxygen binding and activation mechanisms with unprecedented accuracy. Computational spectroscopy allowed for molecular interpretation of the ROS spectroscopic EPR parameters, and their structure sensitivity.

Towards “better” molecular magnets. Correlation of structure and magnetic anisotropy

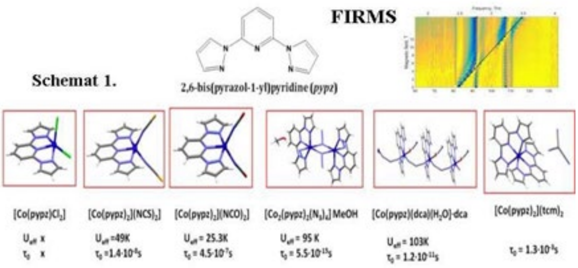
Alina Bieńko

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

alina.bienko@uwr.edu.pl

Key words: magnetic anisotropy; SMM; SIM; HFEPR; FIRMS.

The theoretical and experimental study carried out in recent years allowed to determine the properties that guarantee SMM or SIM type behavior, which are: high spin state S, large magnetic anisotropy with both a negative ZFS parameter D (easy-axis anisotropy) and an easy-plane anisotropy ($D > 0$), as well as the formation of a significant energy barrier (increasing with S and D). These properties lead to bistable systems, showing the longer the relaxation times, the higher the energy barrier. However, since the specific conditions for the occurrence of SMM and SIM are not easy to achieve in practice, and the blocking temperatures of the molecular magnets obtained so far oscillate in a low range, our activities focused on finding a path of “tuning” the values of magnetic parameters. The correlation of the magnetic study with the crystal and molecular structure is the basis for the control of the synthesis and properties of the obtained magnetic materials, and ensures a change in magnetic anisotropy as a result of rational changes in structural anisotropy. However, achieving a high D value requires understanding how to adjust the geometry of the compound to obtain a significant contribution of spin-orbital coupling to magnetic anisotropy. The results of our research work conducted for a series of Co(II) complexes with the different N- donor ligands, its derivatives and halide or pseudohalide linkers show that the modulation of the geometry of the system is possible by modifying structural factors: substituent replacement in the ligand, disturbance of the ligand field strength, introduction of anionic ligands (Scheme 1). The presence of high magnetic anisotropy affecting a significant increase in the energy barrier in the obtained materials was additionally confirmed by high-field EPR (HFEPR) studies in the frequency range of 100-650 GHz supported, due to the large splitting of energy levels, by the innovative FIRMS (Far-Infrared Magnetic Spectroscopy) method consisting in on terahertz frequency sweeps and measurement of radiation absorption as a function of frequency. Our research shows also that not only the negative sign of the D parameter is not a necessary condition to observe relaxation processes, but also no or almost negligible zfs effect or high ground state spin. An example we reported the field induced slow magnetic relaxation in Cu(II), Mn(II) and Cr(III) complexes.



Schemat 1.

Kittel's theory of ferromagnetic resonance for thin, flexible films with embedded magnetic nanostructures

Maciej Marć [a], Wiktor W. Wolak [a], Andrzej Drzewiński [a], Stepan Mudry [b], Ihor Shtablavyi [b], Mirosław R. Dudek [a]

[a] *Institute of Physics, University of Zielona Góra, 4a Szafrana Str., 65-069 Zielona Góra, Poland*
[b] *Department of Metal Physics, Ivan Franko National University of Lviv, 8 Kyrylo & Mephodiy Str., 79005 Lviv, Ukraine*

m.marc@if.uz.zgora.pl; w.wolak@if.uz.zgora.pl; a.drzewinski@if.uz.zgora.pl; stepan.mudryy@lnu.edu.ua; ihor.shtablavyi@lnu.edu.ua; m.dudek@if.uz.zgora.pl

Key words: ferromagnetic resonance; thin film; magnetic nanoparticles; magnetic nanowires.

The intensive development of flexible magnetoelectronics is leading to the appearance of new materials in the form of non-magnetic flexible polymer matrices with embedded densely packed magnetic nanoparticles. These nanoparticles form various types of nanolayers, magnetic nanowires and other magnetic agglomerates forced by the restricted geometry of the thin film, in which magnetic dipole interactions become important. These interactions can be controlled by elastic deformations of the polymer matrix [1]. The densely packed magnetic nanoparticles can be obtained using the physico-chemical methods of 2D printing by forcing the self-assembly of nanoparticles into various types of spatial structures. The example can be magnetic nanowires [2,3]. Magnetic interactions present in the confined geometries significantly affect the ferromagnetic resonance condition. In this research, we show how Kittel's theory [4] can be adapted to describe magnetic resonance in such systems.

Acknowledgments. M.M., W.W., A.D., and M.D. acknowledge funding by the Ministry of Science under the "Regional Excellence Initiative" program, project No. RID/SP/0050/2024/1.

References

[1] Krzysztof K. Dudek, Maciej Marć, Wiktor Wolak, Andrzej Drzewiński, Mirosław R. Dudek, Theoretical concept describing a use of magnetic nanoparticles in a thin elastic film for the detection of mechanical deformation, Phys. Status Solidi B, 258 (2021) 2100162. DOI: 10.1002/pssb.202100162.

[2] Maciej Marć, Wiktor Wolak, Andrzej Drzewiński, Stepan Mudry, Ihor Shtablavyi, Mirosław R. Dudek, The concept of using 2D self-assembly of magnetic nanoparticles for bioassays, Appl. Sci. 14 (2024) 1906. https://doi.org/10.3390/app14051906.

[3] M. Marć, W. Wolak, A. Drzewiński, M. R. Dudek, Coffee-ring formation through the use of the multi-ring mechanism guided by the self-assembly of magnetic nanoparticles, Sci. Rep. 12 (2022) 20131. https://doi.org/10.1038/s41598-022-24521-x.

[4] C. Kittel. On the theory of ferromagnetic resonance absorption, Phys. Rev. 73 (1948) 155–161.

The impact of linker ligands on the structure dimensionality, magnetic anisotropy and slow relaxation processes of six-coordinate Ni(II) complexes

Jacek Sawka[a], Alina Bieńko[a], Anna Świtlcka[b], Roman Boča[c], Andrew Ozarowski[d]

[a] Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
[b] Department of Crystallography, Institute of Chemistry, University of Silesia, 9 Szkolna St., 40-006 Katowice, Poland
[c] Department of Chemistry, Faculty of Naturel Sciences, University of SS Cyril and Methodius, 917 01 Trnava, Slovakia
[d] National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States

jw.sawka@gmail.com; alina.bienko@uwr.edu.pl

Key words: Single-Molecule Magnets (SMM); Single-Chain Magnets (SCM); Magnetic anisotropy; Slow Magnetic Relaxation; Ni(II) complexes.

The search for new functional materials which show magnetic properties typical of molecular magnets (SMM) or single magnetic ions (SIM) such as long relaxation times, spontaneous magnetization below the critical temperature and the ability to tunnel the quantum magnetization has been a challenge for scientists for many years. However, even if suitable condition have been met the obtained compounds still exhibit too low blocking temperature. For this reason, the purpose of our research is finding a path of "tuning" the values of magnetic parameters through structure correlation and magnetic anisotropy, which is measured by the zero field splitting parameter in a zero magnetic field (D). There are many proposed examples of such mechanisms in the literature for Co(II) compounds, while such relationships for Ni(II) ions (with two unpaired electrons and characteristic magnetic anisotropy) are still relatively unknown. Considering the above we present the study of structure and magnetic properties of two Ni(II) complexes with 2.6-bis(pyrazol-1-yl) pyridine ligands and different linker ligands: azide and dicyanoamide about formulas $[Ni_2(pypz)_2(\mu_{1,1}-N_3)_2(N_3)_2]\cdot 2H_2O$ and $[Ni(pypz)(dca)(H_2O)]_n\cdot n(dca)$. The use of various pseudohalide ligands allowed for fine-tuned the magnetic anisotropy and relaxation dynamics by controlling the ligand field strength and symmetry of the crystal field. The presence of high magnetic anisotropy affecting a significant increase in the energy barrier in the obtained materials was additionally confirmed by high-field EPR (HFEPR) measurement in the frequency range of 100-650 GHz due to the large splitting of energy levels. The AC susceptibility of complex $[Ni_2(pypz)_2(\mu_{1,1}-N_3)_2(N_3)_2]\cdot 2H_2O$ indicates multiple relaxation processes, analyzed via the Debye model, revealing parameters indicative of Raman and direct relaxation processes.

Study of Catalytic Systems by Electron Paramagnetic Resonance Spectroscopy

Krzysztof Kruczała,[a] Radim Beranek,[b] Szymon Wierzbicki[a]

[a] *Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland*
[b] *Institute of Electrochemistry, Ulm University, Albert-Einstein-Allee 47, 89069 Ulm, Germany*

krzysztof.kruczala@uj.edu.pl

Key words: photocatalyst; spin trap; zeolites; oxygen reduction reaction.

Electron paramagnetic resonance (EPR) spectroscopy is a method of choise to study species with unpaired electrons, such as transition metal cations, reactive oxygen species (ROS), adsorbed radical anions, and defects, which are often involved in catalytic reactions. In this talk, some examples of the application of EPR to the study of heterogeneous catalytic systems will be presented. The in situ measurements performed with a micro-AEMFC placed in the cavity of the EPR spectrometer allowed the detection of •OOH and •OH radicals on the cathode side and •H radicals on the anode side (Fig. 1). The presence of such radicals indicates that ROS play an important role in the degradation mechanism of the anion-conducting polymers [1]. In the case of the photocatalysts, it was possible to determine the location of VO^{2+} (Fig. 2) and Cu^{2+} ions in the TiO^{2} matrix and to follow the evolution of the redox center during the catalytic reactions. EPR measurements showed that both cocatalysts enhance the activity of the catalysts, but the mechanism of enhancement is different in both cases [2]. EPR spectroscopy provides evidence for the highly dispersed state of ceria throughout the zeolite matrix and the presence of superoxide radicals [3].

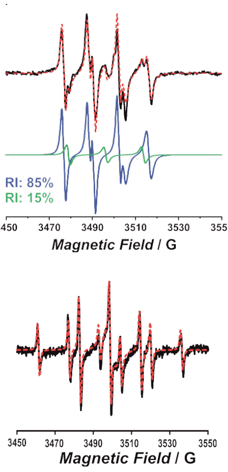


Fig. 1. Experimental (black) and simulated (red) EPR spectra of DMPO-OOH and DMPO-H adducts detected in AEMFCs

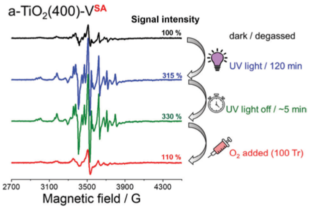


Fig. 2. In situ X-band EPR spectra of a-TiO2(400) -V^{SA} upon UV irradiation

The examples presented here illustrate the great power of EPR in studying the catalytic system as well as the mechanisms of catalytic reactions.

References

[1] S. Wierzbicki, J.C. Douglin, R.K. Singh, D.R. Dekel*, K. Kruczała*, *ACS Catalysis*, 13(4) (2023) 2744-2750.
[2] K. Kruczała*, S. Neubert, K. Dhaka, D. Mitoraj, P. Jánošíková, Ch. Adler, I. Krivtsov, J. Patzsch, J. Bloh, J. Biskupek, U. Kaiser, R.K. Hocking, M.C. Toroker*, R. Beranek*, *Advanced Science*, 35 (10) (2023) 2303571.
[3] K. Gołąbek, A.E Palomares, J. Martínez-Triguero, K.A. Tarach, K. Kruczała, V. Girman, K. Góra-Marek, *Applied Catalysis B: Environmental*, 259 (2019) 118022.

Acknowledgements. This work was partially supported by the Polish National Science Centre (NCN) project OPUS-14, No. 2017/27/B/ST5/01004.

Metal Cation Radical Complexes: From Environmental Pollutants to Functional Materials

Maciej Witwicki[a]

[a]*University of Wroclaw, Faculty of Chemistry, ul. Joliot-Curie 14, 50-383 Wroclaw, Poland*

maciej.witwicki@uwr.edu.pl

Key words: radicals; EPR; high-field EPR; DFT; ab initio.

Radicals are atoms or molecules with an unpaired electron in an orbital with dominant s or p character. Although typically unstable, their stability can be enhanced through steric protection, spin density delocalization or coordination with metal cations, allowing for the isolation of radicals as pure compounds.

Environmentally persistent free radicals (EPFRs) are pollutants that may contribute to health problems. Most studies focus on EPFRs from combustion, but we demonstrated, using multifrequency EPR spectroscopy, that EPFRs can also form from natural polyphenols exposed to heavy metal ions like Pb(II) and Hg(II). Our relativistic DFT computations revealed these radical species are semiquinonato complexes of heavy metal ions.

Radical species have applications in material science. We isolated a stable semiquinonato complex of aluminum from 1,2-dihydroxybenzene and characterized it using multifrequency cw-EPR spectroscopy and computational techniques (DFT and DLPNO-CCSD). Additionally, we synthesized complexes of Al^{3+}, Co^{2+}, Gd^{3+}, and Dy^{3+} with a redox-active pincer O,N,O ligand derived from 3,5-di-tert-butylcatechol for single-molecule magnet (SMM) applications. These complexes with the O,N,O ligand, which can exist in various oxidation states (Fig. 1), were analyzed using X-ray crystallography, multifrequency EPR, SQUID measurements and detailed theoretical calculations (fractional occupation number weighted electron density and CASSCF/NEVPT2).

Acknowledgments. This research was supported by the “Excellence Initiative – Research University” program at the University of Wroclaw (2020-2026). High field EPR spectra were recorded at the National High Magnetic Field Laboratory, supported by National Science Foundation (Cooperative Agreement No. DMR-1644779 and DMR-2128556) and the State of Florida. Computations were performed using Wroclaw Center for Networking and Supercomputing (https://wcss.pl; grant no. 47).

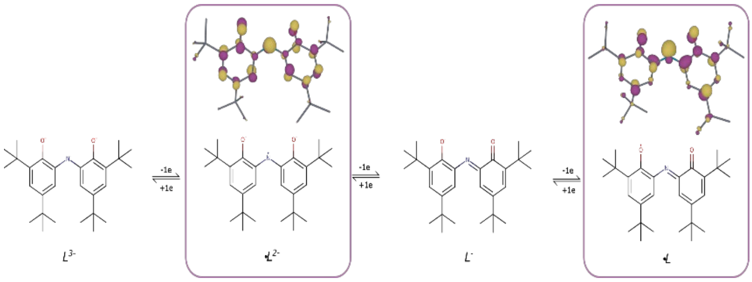


Fig. 1. Oxidation states of the pincer O,N,O ligand used in this study

From dioxygen to superoxide – EPR study of paramagnetic Zn^{2+}-$O_2^{\bullet-}$ species in ZSM-5 zeolite and periodic DFT modeling

Aneta Krasowska[a], Paweł Rejmak[b], Piotr Pietrzyk[a]

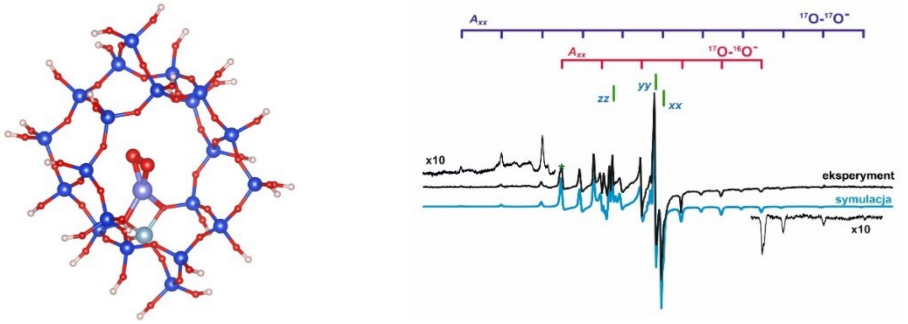
[a] *Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Kraków, Poland*
[b] *Polish Academy of Sciences, Institute of Physics, Lotników 32/46, 02-668 Warszawa, Poland*

Piotr.Pietrzyk@uj.edu.pl

Key words: EPR; DFT; superoxide; oxygen activation; spectra simulations; ZSM-5.

The activation of dioxygen O_2 molecules may involve either electron or energy transfer processes. The latter implies redox transformation leading to reactive oxygen species (ROS). One such species, $O_2^{\bullet-}$ superoxide radical anion, plays a vital role in catalysis, environmental chemistry, and biochemistry. One of the possible ways to generate these radicals is O_2 adsorption on low-valent transition-metal ion centers dispersed in porous materials, such as zeolites. Herein, we present an EPR spectroscopic and theoretical analysis of an excellent example of a system defined by monovalent Zn^+ ions.

This work aims to refine the experimental EPR studies involving the adsorption of isotopically labeled $^{17}O_2$ on Zn^+ exchanged MFI zeolite obtained by chemical vapor deposition. EPR measurements provided geometric constraints for the observed superoxide species, while periodic DFT modeling detailed its structure and electronic properties. The geometry optimization was performed at the DFT level for periodic models of MFI, containing a single Zn^+ ion (Fig. 1) and Zn^+-Zn^{2+} pair, where oxygen adsorption can lead to the formation of $O_2^{\bullet-}$. Several possible zinc-superoxide adducts were computationally studied. Large cluster models were subsequently cut from these structures and used for calculating EPR g and A tensors.



(a) (b)

Fig. 1. (a) DFT-optimized structure of side-on Zn^{2+}-$O_2^{\bullet-}$ with two magnetically equivalent oxygen nuclei, and (b) EPR powder spectra for 17-O enriched adsorption complex (b)

Acknowledgments. This study was supported by the National Science Center (NCN), Poland, Sonata Bis 7 no. 2017/26/E/ST4/00794, partly by PL-Grid infrastructure (ACK Cyfronet).

Identification of reactive oxygen species generated by the interaction of transition metal oxides and H_2O_2

Kamila Sobańska[a], Piotr Pietrzyk[a]

[a] *Jagiellonian University, Faculty of Chemistry, 2 Gronostajowa Str., 30-387 Kraków, Poland*

kamila.sobanska@uj.edu.pl, pietrzyk@chemia.uj.edu.pl

Key words: reactive oxygen species; radicals; hydrogen peroxide; advanced oxidation processes.

From the point of view of catalytic and environmental chemistry, reactive oxygen species (ROS) are extremely important entities containing oxygen atoms in unusual oxidation states or dioxygen in the excited state. These include hydroxyl radicals ($^\bullet$OH), superoxide anions ($O_2^{-\bullet}$) or singlet oxygen ($^1O_2$). ROS can be produced by the Fenton reaction using hydrogen peroxide and photocatalytic processes. Due to the high oxidizing activity of organic pollutants and non-toxicity, they are increasingly used in advanced oxidation processes, which makes them an alternative to commonly used, chemically supported methods of biological and mechanical purification. In fact, AOPs can be used as the last step in the water purification when contaminant concentrations are at a low level. This aspect is there beneficial because the efficiency of AOP processes can be controlled by selecting an appropriate catalyst that enables the formation of significant amounts of strongly oxidizing radicals.

The aim of this work is the identification of reactive oxygen species generated during hydrogen peroxide activation on transition-metal oxides and the relation between composition of the catalyst (type of transition metal, presence of an admixture) and it's activity in oxidation of model organic wastewater pollutants. The materials used in this study (Zr and Nb amorphous oxides and their composites with CeO_2, CuO nanocrystalline phases) were selected in such a way that they enable the formation of ROS via the Fenton and electroprotic mechanisms. In the first step, they were characterized by X-ray diffraction (XRD) and Raman spectroscopy to confirm their structure. EPR spectroscopy, especially measurements using the 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) spin trap and 2,2,6,6-tetramethyl-4-piperidone (TEMP) oxidation, was used to identify paramagnetic ROS such as hydroxyl radicals and singlet oxygen, respectively. In addition, the activity of the catalysts in methylene blue, rhodamine B, and ciprofloxacin degradation as a test reaction was investigated. The obtained results showed synergy between the adsorption of pollutant molecules on the surface of the catalysts and the activity in the formation of ROS and their ability to undergo degradation reactions. Catalysts that generate the largest amount of $^\bullet$OH radicals have the greatest activity in the degradation processes. This is because hydroxyl radicals are responsible for the degradation of dyes.

Acknowledgments. This research was financially supported by the National Science Center, Poland (NCN), grant Sonata Bis7 (no. 2017/26/E/ST4/00794).

The effect of oxidative degradation of Dopa-melanin on its basic physicochemical properties and photoreactivity

Krystian Mokrzyński[a,b], Andrzej Żądło[a], Grzegorz Szewczyk[a], Michał Sarna[a],
Theodore G. Camenisch[d], Shosuke Ito[e], Kazumasa Wakamatsu[e], Tadeusz Sarna[a]

[a] *Department of Biophysics, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Kraków, Poland*
[b] *Department of Biophysics and Cancer Biology, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Kraków, Poland*
[c] *Department of Biophysics, Chair of Physiology, Jagiellonian University Medical College, Kraków, Poland*
[d] *Department of Biophysics, Medial College of Wisconsin, Milwaukee, WI, USA*
[e] *Institute for Melanin Chemistry, Fujita Health University, Toyoake, Aichi 470-1192, Japan*

krystian.mokrzynski@uj.edu.pl

Key words: eumelanin; oxidative degradation; bleaching; singlet oxygen; photoprotection; phototoxicity.

Melanin, particularly eumelanin, is commonly viewed as an efficient antioxidant and photoprotective pigment. Nonetheless, the ability of melanin to photogenerate reactive oxygen species and sensitize the formation of cyclobutane pyrimidine dimers may contribute to melanin-dependent phototoxicity. The phototoxic potential of melanin depends on a variety of factors, including molecular composition, redox state, and degree of aggregation. Using complementary spectroscopic and analytical methods we analyzed the physicochemical properties of Dopa-melanin, a synthetic model of eumelanin, subjected to oxidative degradation induced by aerobic photolysis or exposure to 0.1M hydrogen peroxide. Both modes of oxidative degradation were accompanied by dose-dependent bleaching of melanin and irreversible modifications of its paramagnetic, ion- and electron-exchange and antioxidant properties. Bleached melanin exhibited enhanced efficiency to photogenerate singlet oxygen in both UVA and short-wavelength visible light. Although chemical changes of melanin subunits, including a relative increase of DHICA content and disruption of melanin polymer induced by oxidative degradation were considered, these two mechanisms may not be sufficient for a satisfactory explanation of the elevated photosensitizing ability of the bleached eumelanin. This study points out possible adverse changes in photoprotective and antioxidant properties of eumelanin that could occur in pigmented tissues after exposure to high doses of intense solar radiation.

Benchtop X-band EPR for *in vivo* studies of zebrafish - melanin radicals and nitroxyl spin probes

Katarzyna Zawada [a], Katerina Makarova[a], Małgorzata Korzeniowska nee Wiweger[b]

[a] *Medical University of Warsaw, Faculty of Pharmacy, Department of Organic and Physical Chemistry, Banacha 1 Str., 02-097 Warsaw, Poland*
[b] *Laboratory of Protein Engineering, Mossakowski Medical Research Institute, Polish Academy of Sciences, 5 Pawinskiego Str., 02-106 Warsaw, Poland*

katarzyna.zawada@wum.edu.pl, katerina.makarova@wum.edu.pl, mkorzeniowska@imdik.pan.pl

Key words: zebrafish, melanin radicals, spin probes, membrane fluidity, *in vivo* model.

In vivo studies rarely utilized X-band EPR due to the small size of X-band resonators and the relatively high power required to detect EPR signals, which rendered them unsuitable for most often used laboratory animals such as mice or rats.

Zebrafish (*Danio rerio*) is a small tropical fish with genome sharing over 70% similarity with humans. Relatively easy husbandry, ease of genetic modifications, fast development, and the close mirroring of processes in humans make zebrafish an attractive substitute for other vertebrate models, particularly in biomedical research. Among the wide range of applications, zebrafish are used as a model for cancer, neurodegenerative diseases and ageing, i.e. processes where free radicals play an important role.

To allow an *in vivo* detection of free radicals in living zebrafish embryos and larvae we designed specially-shaped glass and quartz capillaries. When used together with eSpect+, they allow the measurement of X-band EPR spectra while ensuring the embryos and larvae survival.

One of applications of this approach is the detection of a single line EPR spectrum corresponding to eumelanin free radicals naturally forming in zebrafish. The signal is visible in pigmented zebrafish embryos and is absent in the *albino* line, which has a naturally occurring mutation in the *slc45a2* gene that blocks melanin synthesis. Similarly, fish in which pigment formation has been chemically inhibited by phenylthiourea also lack the signal.

Melanin has very diverse roles and functions in various organisms, yet in most species it gives coloration to skin or eyes, and protects from UV radiation. It is also postulated that it plays an important role in melanoma progression. When oxidized, melanin forms radicals, which could be detected with EPR spectroscopy. This application could be expanded by xenotransplanting human melanoma cells into zebrafish embryos giving new opening for melanoma studies.

When using zebrafish model and specially-shaped capillaries together with eSpect+, standard X-band EPR spectrometers can have other *in vivo* applications. The EPR parameters could be used to calculate membrane order parameters and, thus, give direct information about fluidity/rigidity of the membrane *in vivo.* For this purpose, we studied both hydrophilic and lipophilic spin probes. As a result, we were able to detect changes in the membrane fluidity in pigment-free mutant or chemically treated fish.

Two-dimensional magnetism in a self-inercalated transition metal dichalcogenides

M. Kuzma[a], M. Bester[a], B. Cieniek[a], V. Popowich[b], I. Stefaniuk[a]

[a] *University of Rzeszów, College of Natural Sciences, Institute of Physics, S. Pigonia 1,35-959 Rzeszów, Poland*
[b] *Department of Technological and Professional Education, Ivan Franko Drogobych Pedagogical University, 24 Ivan Franko str., 82100 Drogobych, Ukraine*

mkuzma@ur.edu.pl

Key words: 2-D magnetism; chromium tellurides; ferromagnetic resonance.

The layered structure of dichalcogenides $Cr_{1+\delta}Te_2$ facilitates their epitaxial growth with thickness down to 1.2 nm which is equivalent to 2-unit cell thickness of monolayers [1]. In such monolayers, the magnetic anisotropy counteracts spin fluctuations, thereby providing the samples for exploring magnetic properties in the 2D limit. The δ parameter of non-stoichiometry tunes considerable phase transitions in this material. We focus attention on Cr_2Te_3 ($\delta = 0.33$) and Cr_3Te_4 ($\delta = 0.5$) samples (see Fig. 1) for which the Curie temperature approaches a room temperature what is unprecedented opportunity in the field of spintronics.

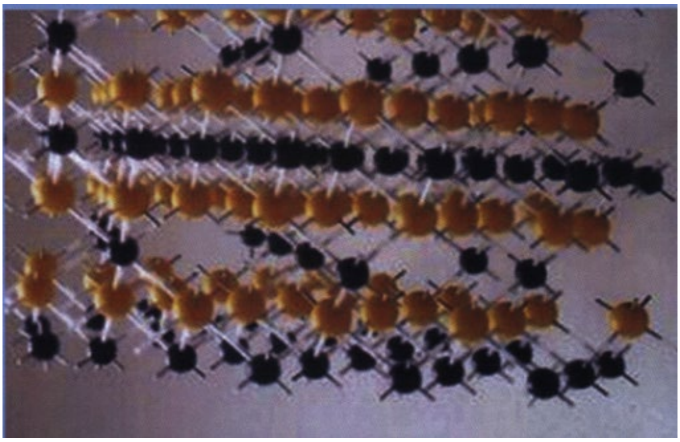


Fig. 1. Model of $Cr_{1+\delta}Te_2$ crystal

The measurements of ferromagnetic resonance in Cr_2Te_3 crystals reveal two types of magnetic transitions. The first at 295 K relates to quasi isolated two–dimensional monolayers with crystal structure of the NiAs type. The second one, at 210 K, follows from bulk ferromagnetism.

References

[1] Y. Fujisawa et al., Tailoring magnetism in self-intercalated $Cr_{1+\delta}Te_2$ epitaxial films, Phys. Rev. Mater. **4** (2020) 114001.

Application of ESR spectroscopy in nanomedicine

Bernadeta Dobosz

Adam Mickiewicz University in Poznań, Faculty of Physics, Functional Materials Physics Division,
2 Uniwersytetu Poznańskiego Str., 61-614 Poznań, Poland

benia@amu.edu.pl

Key words: iron oxide nanoparticles; polymers; yeast cells; cancer cells; targeted therapy.

Despite the development of technology, the diagnostics of many diseases, including cancer, at an early stage and thus the possibility of curing them is still a challenge for medicine. The solution to this problem may be the use of nanomaterials, which, due to widespread interest and extensive research, are gaining increasingly better parameters. Properly prepared nanoparticles can improve the effectiveness of radiotherapy (radiosensitizers) as well as protect healthy tissues and cells (radioprotectors). Functionalized with various drugs (nanodrugs) can be used in targeted therapy, which will also improve the effectiveness of treatment while reducing the dose of the drug. The potential effectiveness of such a solution is influenced by many factors, related to both the properties of the material itself and the purpose of its use (e.g. tumor environment). Such studies are performed using cell lines and tissue models.

Iron oxide and polymer nanoparticles were investigated using electron spin resonance spectroscopy (ESR). The measurements were performed on a Bruker ESR spectrometer EMX-10, operating in the X-band (9.4 GHz). The nanoparticles were functionalized with nitroxide probes, TEMPO derivatives. The research used yeast cells as a model organism and selected cancer cell lines. Cell proliferation was monitored under a microscope. The received results show the wide possibility of using the ESR technique in nanomedicine and also indicate what should be particularly noted in this type of research.

EPR case study - tracking long-lived free radicals in dandelion caused by air pollution

Ireneusz Stefaniuk [a], Bogumił Cieniek [a], Agata Ćwik [b], Katarzyna Kluska [c], Idalia Kasprzyk [c]

[a] *University of Rzeszów, Institute of Materials Engineering, Pigonia 1, Rzeszów 35-939, Poland*
[b] *University of Rzeszów, Institute of Agricultural Sciences, Environment Management and Protection, Zelwerowicza 8B, Rzeszów 35-601, Poland*
[c] *University of Rzeszów, Institute of Biology, Zelwerowicza 4, Rzeszów 35-601, Poland*

istefaniuk@ur.edu.pl; bcieniek@ur.edu.pl; acwik@ur.edu.pl; kborycka@ur.edu.pl; ikasprzyk@ur.edu.pl

Keywords: Taraxaum sp.; dandelion; free radicals; air pollution; EPR.

Particulate air pollution is one of the global environmental pollutants. Studies indicate that a new type of pollutant from mainly fossil fuel combustion and automobile exhaust emissions should be considered, i.e. environmentally persistent free radicals (EPFRs). These radicals are ubiquitous in the environment, have a long life span, and are capable of producing harmful reactive oxygen species (ROS). Dandelion is a plant that is often used for biomonitoring.

The samples were collected in 2020 and 2021 in spring and late summer on rain-free days. The material used for the study was roots, leaves, flower stalks and inflorescences of Taraxaum sp., and was collected from 6 sites with 3 plants each. The air pollution of particulate matter with PM10 and PM2.5 fractions was also measured using a DustTrak II analyzer. The content of EPFRs in dandelions was studied using the electron paramagnetic resonance (EPR) method. Two types of radicals were considered, for values of g factor < 2.0030 associated to C-centered radicals, and for g factor > 2.0030 associated with a mixture of O- and C- centered radicals. Relationships between components were also determined for each part of the plant. The leaf was selected as the most appropriate part of the plant for the measurement of carbon-derived EPFRs radicals. The g_{ef} value (Fig. 1) and the total number of spins were performed. The results obtained from the EPR measurements and air pollution were analyzed and relationships between location, season, and EPR results were found.

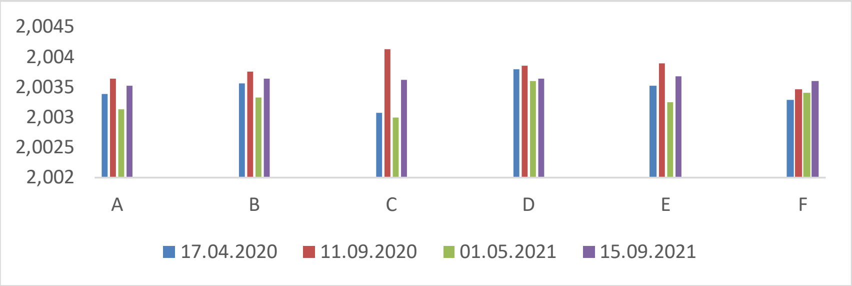


Fig. 1. Average g_{ef} values for the leaf for the position and intake periods

Acknowledgment. This research was supported by the Minister of Science of the Republic of Poland under the Programme “Regional initiative of excellence”. Agreement No. RID/SP/0010/2024/1.

Photoinduced processes on modified titanium dioxide photocatalysts studied by indirect cw-EPR techniques

Zuzana Dyrčíková [a], Miriama Malček Šimunková [a], Dana Dvoranová [a]

[a] *Slovak University of Technology in Bratislava, Faculty of Chemical and Technology, Institute of Physical Chemistry and Chemical Physics, Radlinského 9, SK-812 37 Bratislava, Slovak Republic*

zuzana.dyrcikova@stuba.sk; miriama.simunkova@stuba.sk; dana.dvoranova@stuba.sk

Key words: photocatalysis; spin trapping; photoinduced electron transfer; reactive oxygen species.

Heterogeneous photocatalysis, as one of the advanced oxidation processes (AOPs), is an exciting strategy in the lowering of an increasing stress on the environment due to expanding needs of civilization place. The key restriction so far has been the selection of the right photocatalyst, as existing semiconductor photocatalysts are mostly employed when exposed to UV light. The target is expansion of their photocatalytic effectiveness into the visible region and preparation of the sunlight-driven photocatalyst. Different approaches from several semiconductor materials have already been presented. Composite photocatalysts are formed by doping with metallic and non-metallic portions, resulting in the production of complexes with interfacial charge transfer (ICT). Based on a mixture of quantum chemical calculations and prior experiments, the development of ICT complexes looks to be a viable avenue. The combination of organic molecules (*e.g.*, taxifolin, salicylic acid derivatives) on the surface of the semiconductor allows photoinduced charge carriers to be transferred from the organic molecules to the semiconductor photocatalyst, preserving their potential and potentially leading to the formation of reactive oxygen species that participate in degradation reactions. Spectroscopic methods such as cw-EPR and UV-Vis-NIR spectroscopy allow a unique view of ongoing processes in various systems. Thanks to indirect EPR techniques such as spin trapping with 5,5-dimethyl-1-pyrolline *N*-oxide (DMPO), spin scavenging with 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Tempol) or photoreduction *via* reduction semi-stable radical cation of 2,2′-azinobis-(3-ethylbenzthiazolin-6-sulfonate) is possible to utilize the photocatalytic properties of nanomaterials in various environments. Based on the results so far, it can be said that compared to the pure semiconductor photocatalyst, the photocatalytic efficiency in the visible region has improved [1-5].

Acknowledgments. This study was financially supported by the Slovak Research and Development Agency under the contracts Nr. APVV-19-0024 and Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0422/24).

References

[1] V. Nikšić, M., Malček Šimunková, Z. Dyrčíková, et al., Opt. Mater. 152 (2024) 115454.

[2] Z. Barbieriková, D. Dvoranová, V. Brezová, et al., Opt. Mater. 89 (2019) 237.

[3] Z. Barbieriková, M. Šimunková, V. Brezová, et al., Opt. Mater. 123 (2022) 111918.

[4] Z. Barbieriková, D. Dvoranová, V. Brezová, Mat. Sci. Photocat., Elsevier, Ch. 8, (2021) 125.

[5] D. Dvoranová, Z. Barbieriková, V. Brezová, Molecules, 18 (2014) 17279.

Herbs with antioxidant and photosensitizing properties

Zuzanna Didjurgeit, Iga Sienkiewicz, Adrianna Kędziora, Beata Kucharska, Bernadeta Dobosz

Functional Materials Physics Division, Faculty of Physics, Adam Mickiewicz University, Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland

zuzdid@st.amu.edu.pl; igasie1@st.amu.edu.pl

Key words: photosensitizers; herbs; antioxidants; photodynamic therapy; TEMPO.

Photosensitization is a process that increases the skin's sensitivity to sunlight. It may be caused by active compounds contained in medicinal plants. This mechanism is also used in photodynamic therapy (PDT), which involves the use of photosensitizers activated by light of an appropriate wavelength. Photodynamic therapy is used in the treatment of various diseases, including skin cancer. Many photosensitizing herbs also have antioxidant properties, making them interesting from a medical perspective. The aim of the study was to assess the antioxidant properties of selected photosensitizing herbs using the electron paramagnetic resonance (EPR) technique. The study included chamomile, horsetail, goldenrod, and lovage. The EPR technique enabled the registration of spectra, based on which changes in the concentration of free radicals over time were measured. The experiment used the TEMPO nitroxide radical, to which infusions of the tested herbs were added. The results of the EPR analysis confirmed that all tested herbs have the ability to scavenge free radicals, with varying degrees of effectiveness. The conducted research highlights the potential of these plants as natural antioxidants, but their photosensitizing properties require further research in the context of use during photodynamic therapy.

System of digital scanning of the magnetic field for radiospectrometers of the "RADIOPAN" company (Poznań, Poland)

Vasyl Tataryn[a], Bohdan Padlyak[b,c], Oleksiy Tataryn[d]

[a] Lviv Polytechnic National University, Institute of Computer Technologies, Automation and Metrology, 28a Bandery str. 79013 Lviv, Ukraine
[b] University of Zielona Góra, Institute of Physics, 4a Prof. Szafrana Str., 65-516 Zielona Góra, Poland
[c] Ivan Franko National University of Lviv, Vlokh Institute of Physical Optics, 23 Dragomanov Str., 79005 Lviv, Ukraine
[d] Odesa Polytechnic National University, 1 Shevchenko Str., 28010 Odesa, Ukraine

vasyl.y.tataryn@lpnu.ua; B.Padlyak@if.uz.zgora.pl; otataryn@gmail.com.

Key words: RADIOPAN company; EPR; modernization; digital NMR magnetic field unit; sensitivity.

In order to provide high resolution and sensitivity EPR spectrometers are quite bulky devices, because they use large magnets to ensure the homogeneity of magnetic field in the investigated sample. The EPR spectrometers have been manufactured since the discovery of the EPR phenomenon until to the present time by different producents. It is natural that some part of the electronic equipment of old EPR spectrometers are physically and technically obsolete. Whereas the magnet itself and the microwave bridge remained practically unchanged up to now.

Modernization of the "RADIOPAN" EPR spectrometers firstly was solved by using a digital magnetic field scan unit, described in [1]. The proposed in [1] magnetic field scan unit linearly changes magnetic field and measures its value. Such solution allows significantly expand technical capabilities of the "RADIOPAN" EPR spectrometers, but does not use their construction features. In our opinion during modernization of the EPR spectrometers must be maximally taking into account their construction features.

All "RADIOPAN" EPR spectrometers contain NMR magnetometer of high quality, which can be used for precise magnetic field measurements. and to carry out the field sweeping by using the same standard magnet current amplifier to the input of which is applied a voltage corresponding to desired value of the magnetic field. Thus, the magnetic field values can be directly read from the NMR unit of the "RADIOPAN" EPR spectrometer that allows to record the magnetic resonance signal with high resolution.

Proposed modernization of the "RADIOPAN" EPR spectrometer of the SE/X-2544 type was realized in the Institute of Physical Optics (Lviv, Ukraine).

Acknowledgment. Presentation of this work in the VII Forum EMR-PL was supported by the Institute of Physics of the University of Zielona Góra (Poland).

References

[1] Duchiewicz J., Dobrucki A., Francik A., Sadowski A., Oleś T., Duchiewicz T.: The 2-channel EPR spectrometer Radiopan SE/X-254x for relative quantitative measurements. Elektronika – Konstrukcje, Technologie, Zastosowania, Nr 11/2011.

Effect of low concentrations of nitroxides on SH-SY5Y cells transfected with the Tau protein

Kacper Kut [a], Bogumił Cieniek [b], Ireneusz Stefaniuk [b], Grzegorz Bartosz [a], Izabela Sadowska-Bartosz [a]

[a] *University of Rzeszow, College of Natural Sciences, Institute of Food Technology and Nutrition, Laboratory of Analytical Biochemistry, 4 Zelwerowicza Str., 35-601Rzeszow, Poland*
[b] *University of Rzeszow, College of Natural Sciences, Institute of Materials Engineering, 1 Prof. S. Pigonia Str., 35-310 Rzeszow, Poland*

kacperkut@onet.pl; bcieniek@ur.edu.pl; istefaniuk@ur.edu.pl; gbartosz@ur.edu.pl; isadowska@ur.edu.pl

Key words: antioxidant; glutathione; nitroxides; oxidative stress; reactive oxygen species; SH-SY5Y cells

Nitroxides, stable synthetic free radicals, are promising antioxidants, showing many beneficial effects both at the cellular level and in animal studies. However, the cells are usually treated with high millimolar concentrations of nitroxides, which are not relevant to the concentrations that could be attained *in vivo*. This study aimed to examine the effects of low (≤10 μM) concentrations of three nitroxides, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), 4-hydroxy-TEMPO (TEMPOL) and 4-amino-TEMPO (TEMPAMINE), in pure chemical systems and on SH-SY5Y cells transfected with the human tau protein (TAU cells), a model of chronic cellular oxidative stress, and transfected with the empty plasmid (EP cells). All nitroxides were active in standard antioxidant-activity tests except for the 2,2'-azinobis-(3-ethylbenzthiazolin-6-sulfonate) radical ($ABTS^{\bullet}$) decolorization assay. Nitroxides reduced Fe^{3+}, inhibited autoxidation of adrenalin as well as pyrogallol, and oxidation of dihydrorhodamine123 by 3-morpholino-sydnonimine (SIN-1). TEMPO protected against fluorescein bleaching from hypochlorite, but TEMPAMINE enhanced the bleaching, apparently due to chloramine formation. Nitroxides showed no significant cytotoxicity and were reduced by the cells to non-paramagnetic derivatives. They decreased the level of reactive oxygen species, depleted glutathione, and increased mitochondrial-membrane potential in both types of cells, and increased lipid peroxidation in TAU cells. These results demonstrate that even at low micromolar concentrations nitroxides can affect the cellular redox equilibrium and other biochemical parameters.

Funding Statement

This research was performed within the project "Nanomolecular antioxidants: biological basis of targeted therapy of neurodegenerative diseases" (number of the application 2016/22/E/NZ7/00641) financed by the National Science Centre (NCN), Poland, within the "SONATA-BIS 6" program.

Electron magnetic resonance of Co-doped $BaTiO_3$ ceramics at helium temperatures

Łukasz Dubiel [a], Antoni Żywczak[b], Andrzej Wal[c], Ireneusz Stefaniuk [d]

[a] *Department of Physics and Medical Engineering, Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, Powstańców Warszawy 12, 35-959 Rzeszów, Poland*
[b] *Academic Centre for Materials and Nanotechnology, AGH University of Kraków, al. Adama Mickiewicza 30, 30-059 Kraków, Poland*
[c] *Institute of Physics, College of Natural Sciences, University of Rzeszów, 1 Pigonia St., 35-317 Rzeszów, Poland*
[d] *Institute of Materials Engineering, College of Natural Sciences, University of Rzeszów, 35-310 Rzeszów, Poland*

l.dubiel@prz.edu.pl

Key words: $BaTiO_3$; perovskite; multiferroics; Co-doping.

Multiferroics are the subject of intensive studies due to their potential applications in microelectronic or optoelectronic devices. The $BaTiO_3$ perovskite is very interesting due to its multifunctional properties, such as its piezoelectric and ferroelectric [1].

In this poster, we present the results of electron magnetic resonance (EMR) studies on the Co-doped $BaTiO_3$ ceramics for the $BaTiO_3$:Co sample with different cobalt content. The EMR spectra were performed at the 6 – 100 K temperature range.

References

[1] Renata Bujakiewicz-Koronska, Łukasz Gondek, Leonid Vasylechko, et al. Magnetoelectric, spectroscopic, optical and elastic properties of Co-doped $BaTiO_3$ ceramics. J. Alloys Compd. 946 (2023) 169344.

EMR study of spinel multi-shell $CoFe_2O_4$ nanoferrites

Bogumił Cieniek[a], Ireneusz Stefaniuk[a], Magdalena Kulpa-Gresztą[b], Anna Tomaszewska[b], Robert Pązik[b]

[a] *University of Rzeszów, Institute of Materials Engineering, Pigonia 1, Rzeszów 35-939, Poland*
[b] *University of Rzeszów, Institute of Biotechnology, Pigonia 1, Rzeszów 35-939, Poland*

bcieniek@ur.edu.pl; istefaniuk@ur.edu.pl; mkulpa@ur.edu.pl; atomaszewska@ur.edu.pl; rpazik@ur.edu.pl

Keywords: nanoferrites; spinels; EMR; ferrites; magnetic properties.

A ferrites are a ceramic material made up of iron oxide with a metallic element. Ferrite-type compounds described with the general chemical formula AFe_2O_4, where the metal cation A can be commonly represented by the Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, etc. are a fairly broad subgroup of inorganic materials belonging to the larger spinel family, which are depicted by the cubic crystal structure assigned to the Fd¯3 m (No. 227) space group.

Nanoferrites have been prepared using a non-hydrolytic approach through thermal decomposition of the respective zinc, manganese and iron acetylacetonate complexes in a benzyl alcohol at 200°C under a protective atmosphere of N_2. The results of the X-band electron magnetic resonance measurements of $CoFe_2O_4$ nanoferrites were obtained for a wide temperature range (Fig. 1). We can observe complex interactions in the materials being studied. By modifying the composition of the materials it is possible to control the magnetic properties (ferromagnetism-antiferromagnetism-ferrimagnetism).

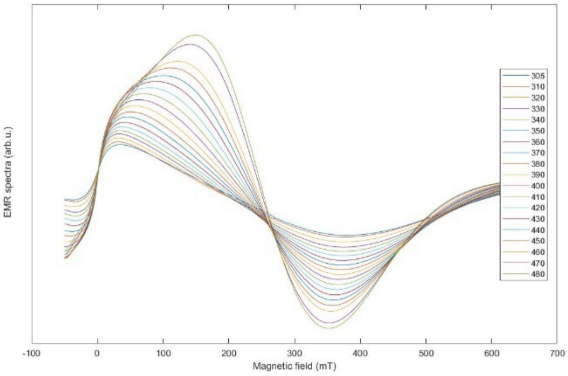


Fig. 1. Temperature dependence of EMR spectra of the $CoFe_2O_4$-Co-Mn-Zn core/shell nanoferrites

EPR and optical spectroscopy of lithium tetraborate glasses doped with Tb and co-doped with Tb and Ag

Ihor Kindrat [a], Bohdan Padlyak [a,b], Adam Drzewiecki [a], Volodymyr Adamiv [b], Ihor Teslyuk [b], Bogumił Cieniek [c], Ireneusz Stefaniuk [c]

[a] *University of Zielona Góra, Institute of Physics, 4a Szafrana Str., 65-516 Zielona Góra, Poland*
[b] *Ivan Franko National University of Lviv, Vlokh Institute of Physical Optics, 23 Dragomanov Str., 79005 Lviv, Ukraine*
[c] *University of Rzeszów, Institute of Materials Engineering, 16a Rejtana Str., 35-310 Rzeszów, Poland*

I.Kindrat@if.uz.zgora.pl; B.Padlyak@if.uz.zgora.pl; A.Drzewiecki@if.uz.zgora.pl; adamiv@ifo.lviv.ua; teslyuk@ifo.lviv.ua; bcieniek@ur.edu.pl; istefaniuk@ur.edu.pl

Key words: lithium tetraborate; Tb^{3+} ions; Ag^{+} ions; Ag nanoclusters; photoluminescence; energy transfer.

The spectroscopic and luminescent properties of the Tb-doped and Tb-Ag co-doped lithium tetraborate ($Li_2B_4O_7$ or $Li_2O–2B_2O_3$) glasses containing 1.0 mol.% Tb_2O_3 and 2.0 mol.% $AgNO_3$ are detailed studied using electron paramagnetic resonance (EPR), optical absorption, and photoluminescence (emission, excitation, decay kinetics, quantum yield) techniques.

The EPR spectra of $Li_2B_4O_7$:Tb glass show signals related to paramagnetic Tb^{4+} ($4f^7$, $^8S_{7/2}$) centres in sites with strong rhombic distortion [1,2] and Fe^{3+} ($3d^5$, $^6S_{5/2}$) non-controlled impurity ions. In the $Li_2B_4O_7$:Tb,Ag glass besides Fe^{3+} ions are observed EPR signals of Ag^0 ($4d^{10}5s^1$) and Ag^{2+} ($4d^9$) ions as well as signal of Tb^{4+} centres in sites with weak rhombic distortion [1,2].

The optical absorption spectra of the investigated glasses show narrow and very weak $4f – 4f$ absorption bands related to Tb^{3+} ($4f^8$, $^7F_6$) ions. The luminescence emission spectra of the both investigated glasses show numerous narrow emission bands corresponding to the $^5D_4 \rightarrow {}^7F_J$ (J = 6 – 0) and $^5D_3 \rightarrow {}^7F_J$ (J = 5 – 3) transitions of Tb^{3+} ions. The decay kinetics of the most intense emission band of Tb^{3+} ions at 541 nm ($^5D_4 \rightarrow {}^7F_5$ transition) is characterised by a lifetime slightly longer than 2.6 ms. The luminescence emission spectra of the Tb-Ag co-doped glass show two broad weakly-resolved emission bands in the violet-green spectral range related to Ag^{+} ($4d^{10}$, $^1S_0$) ions and non-plasmonic Ag nanoclusters (Ag_m^{n+} centres). The decay kinetics of these bands is non-monoexponential, characterised by an average lifetime in the µs time range. An enhancement of the Tb^{3+} luminescence intensity and quantum yield was observed in the Tb-Ag co-doped $Li_2B_4O_7$ glass in comparison with the Tb-doped $Li_2B_4O_7$ glass. The energy transfer from Ag^{+} ions and Ag nanoclusters to Tb^{3+} ions was discussed. Silver co-doping is a promising approach to improve the luminescent properties of Tb^{3+} ions in borate glasses.

Acknowledgements. This work is supported by the Ministry of Education and Science of Ukraine (project number 0122U001833) and the National Science Centre of Poland (project number DEC-2023/07/X/ST3/00737).

References

[1] H. Ebendorff-Heidepriem, D. Ehrt, J. Phys.: Condens. Matter 11 (1999) 7627–7634.

[2] C.M. Brodbeck, L.E. Iton, J. Chem. Phys. 83 (1985) 4285–4299.

Properties of Cd$_{1-x}$Mn$_x$Te as a room temperature semiconductor radiation detector

Iwona Rogalska[a,b], Bogumił Cieniek[a], Ireneusz Stefaniuk[a], Marta Ruszała[a], Jakub Grendysa[a,b], Anna Juś[a]

[a] *University of Rzeszow, Institute of Materials Engineering, Pigonia 1, Rzeszow 35-939, Poland*
[b] *Polish Academy of Sciences, Institute of Physics, International Research Centre MagTop,*
32/46 Lotników Avenue, 02-668 Warsaw, Poland

iwrogalska@ur.edu.pl; bcieniek@ur.edu.pl; istefaniuk@ur.edu.pl; mruszala@ur.edu.pl; ajus@ur.edu.pl; jgrendysa@ur.edu.pl

Keywords: EMR; CdMnTe; MBE; radiation detector; DMS.

The unique features, such as giant Zeeman splitting and bound magnetic polaron (BMP) due to the strong exchange interaction between the magnetic moments of the magnetic ions and the spins of band electrons, of diluted magnetic semiconductors (DMS) have opened the doors for spintronic device applications. In our work, we presented the results of the X-band electron magnetic resonance (EMR) measurements of Cd$_{1-x}$Mn$_x$Te doped with different concentrations of manganese (x – 0.034; 0.046, 0.0112, 0.023, 0.041; measured by XRF method) studied for a wide temperature range. Cd$_{1-x}$Mn$_x$Te have been prepared by molecular beam epitaxy (MBE), to which the end conditions of growth on (100) low-symmetry surface of a substrate had to be first established. Growth processes were performed in the Riber Compact 21 MBE system using the standard MBE growth mode. The crystal structure was evaluated by means of the high-resolution X-ray diffraction technique (HXRD). Using PANalytical's "Amass" program, numerical simulations were conducted to ascertain the composition and thickness of the layers. Cd$_{1-x}$Mn$_x$Te samples are inspected by optical microscopy immediately after unloading from the growth system. In particular, the Nomarski contrast imaging mode is typically utilized, as it offers high resolution and clarity relative to other imaging modes when inspecting thin film samples.

We observed two groups of lines: originating from manganese (330 mT) and a low-field microwave absorption line (LFMA). In addition, we observe a line from other paramagnetic centers (e.g. defects). The subject of our analysis is the line originating from manganese and its dependence on concentration.

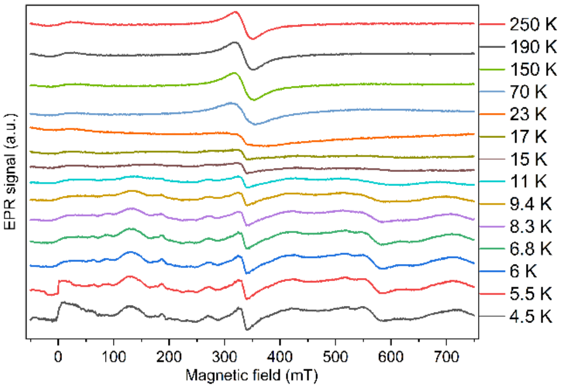


Fig. Temperature dependence of EPR spectra of Cd$_{1-x}$Mn$_x$Te (D353C13, x=0.034)

Temperature dependence of EPR spectra in titanium dioxide modified with (3-aminopropyl) triethoxysilane (APTES)

Danuta Piwowarska[1], Niko Guskos[1], Konstantinos Aidinis [2], Ewelina Kusiak-Nejman[3], Agnieszka Wanag[3], Antoni W. Morawski[3]

[1] West Pomeranian University of Technology in Szczecin, Faculty of Mechanical Engineering and Mechatronics, al. Piastow 19, 70-310 Szczecin, Poland

[2] Department of Electrical and Computer Engineering, Ajman University, Ajman P.O. Box 346, United Arab Emirates

[3] West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, Department of Inorganic Chemical Technology and Environment Engineering, Pułaskiego 10, 70-322 Szczecin, Poland

danuta.piwowarska@zut.edu.pl; nguskos@zut.edu.pl; k.aidinis@ajman.ac.ae; ewelina.kusiak@zut.edu.pl; agnieszka.wanag@zut.edu.pl; antoni.morawski@zut.edu.pl

Keywords: EPR measurements; APTES-modified TiO_2.

Titania nanocomposites modified with 500 mM (3-aminopropyl) triethoxysilane (APTES) were prepared using the solvothermal method (180 °C for 4 h), followed by calcination at higher temperatures (800-1000°C). Modifying titania with APTES has been found to lead to enhanced photocatalytic properties compared with unmodified TiO_2 calcined at the same temperatures. This was attributed to the effective slowing down of the phase transition from anatase to rutile. Electron paramagnetic/ferromagnetic resonance measurements showing EPR spectra from oxygen defects in all nanocomposites (Fig. 1) were strongly dependent on the calcination temperature. Additional resonance lines appeared from magnetic agglomerates whose intensity increased with increased calcination temperature.

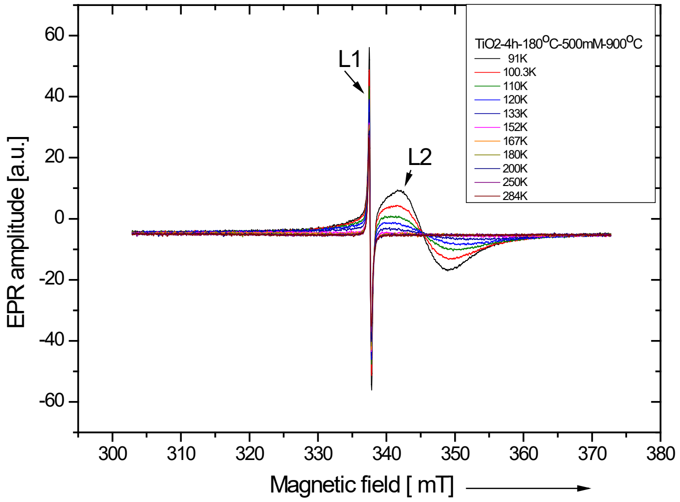


Fig. 1. Temperature dependence of the EPR spectra for nanocomposite of the TiO_2-4h-180°C-500mM- 900°C in the temperature range 90<T<295 K

Spin qubit pairs in DNA Hairpins – EPR methods of study

T. Jasiński[a], M. Drąg[a], M. Kuzma[b]

[a]*Department of Physics and Medical Engineering, The Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, al. PowstańcówWarszawy 6, 35-959 Rzeszów, Poland,*

[b]*University of Rzeszów, College Natural Sciences, Institute of Physics, S. Pigonia 1 Str., 35-959 Rzeszów, Poland*

jasinski@prz.edu.pl; mkuzma@ur.edu.pl

Key words: qubits; hairpin DNA; EPR; initial state.

Deoxyribonucleic acid (DNA) is the well-known biological molecule on which the genetic information of all living organisms from plants to viruses, bacteria to animals and humans is encoded. DNA not only encodes the necessary information for all cells, but also plays an essential role in the formation of all proteins and enzymes for these cells. Synthetically obtained short DNA chains (from a few to several pairs of nucleotides) are called Hairpin DNA (H-DNA) because of the characteristic shape of such a double DNA chain (Fig. 1).

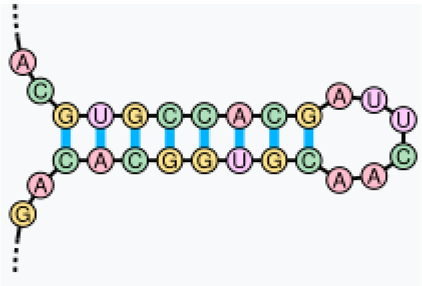


Fig.1. Hairpin DNA.

A peculiar application of H-DNA could be to use this molecule as material for the construction of A a qubit, i.e. the basic unit in a quantum computer corresponding to a bit in classical computers. There are several proposals for the construction of a qubit (e.g. nitrogen defects in diamond). However, a qubit constructed from DNA would have an advantage over the others because it has a well-defined initial state.

In this paper, we will review the basic methods using EPR spectroscopy to study and characterise photogenerated biradicals in DNA Hairpins. Continuous wave methods as well as pulsed methods in the X-band will be analysed.

INDEX OF AUTHORS