Izskaidrota molibdātu un volframātu lokālās atomārās struktūras ietekme uz to termohromiskām un magnētiskām īpašībām

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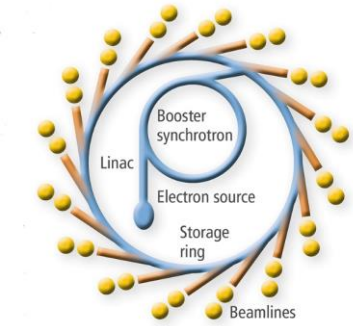
EXAFS Lab

INTRODUCTION (I)

Today, every scientist has the opportunity to use large-scale research infrastructure to perform their state-of-the-art research. In particular, high-quality measurements at **synchrotrons** using various experimental methods can be done.

Combined with experimental methods available in laboratories and high-performance computing, this opportunity opens up unprecedented possibilities for characterizing the structure and properties of materials.

Imaging & Spectroscopy & Scattering



State-of-the-art experiment backed by a solid theory is the key to success!

INTRODUCTION (II)

In this work, we used synchrotron radiation to study a group of smart materials - **molybdates** and **tungstates** (ABO_4) - by X-ray absorption and related spectroscopic methods with the support of advanced simulations.

- The relationship between the local structure distortion and lattice dynamics of molybdates ($CuMoO_4$, $CuMo_{1-x}W_xO_4$, $Cu_{1-x}Zn_xMoO_4$) and their **thermochromic properties** at low and high temperatures has been **revealed and explained**.
- The presence of **magnetic dimers** has been **discovered** in tungstates with high nickel content ($Zn_xNi_{1-x}WO_4$), and their origin was related to the location of nickel ions in the double-well potential.

PUBLICATIONS

The obtained results have been published in **10** peer-reviewed articles during 2018-2021 (5 in 2021).
Three articles have been published in the high-impact journal ***Acta Materialia*** with **IF=8.203** & **SNIP=2.928**.

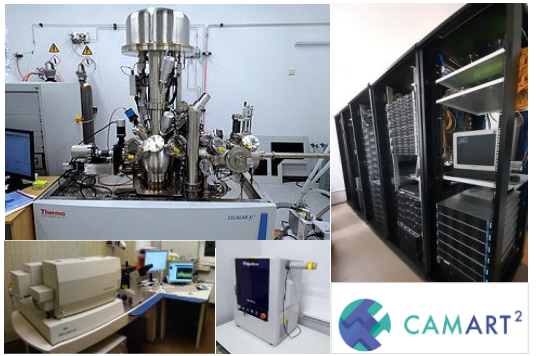
1. I. Pudza, A. Kalinko, A. Cintins, A. Kuzmin, Study of the thermochromic phase transition in $CuMo_{1-x}W_xO_4$ solid solutions at the W L_3-edge by resonant X-ray emission spectroscopy, Acta Mater. 205 (**2021**) 116581. **IF=8.203**
2. G. Bakradze, A. Kalinko, A. Kuzmin, Evidence of dimerization of nickel ions in $NiWO_4$ and $Zn_cNi_{1-c}WO_4$ solid solutions probed by EXAFS spectroscopy and reverse Monte Carlo simulations, Acta Mater. 217 (**2021**) 117171. **IF=8.203**
3. I. Jonane, A. Anspoks, G. Aquilanti, A. Kuzmin, High-temperature X-ray absorption spectroscopy study of thermochromic copper molybdate, Acta Mater. 179 (2019) 26. **IF=8.203**
4. G. Bakradze, A. Kalinko, A. Kuzmin, Chemical-state analysis of Ni, Zn, and W ions in $Zn_cNi_{1-c}WO_4$ solid solutions, J. Phys. Chem. Solids 161 (**2022**) 110425. **IF=3.995**
5. I. Pudza, A. Anspoks, A. Cintins, A. Kalinko, E. Welter, A. Kuzmin, The influence of Zn^{2+} ions on the local structure and thermochromic properties of $Cu_{1-x}Zn_xMoO_4$ solid solutions, Mater. Today Commun. 28 (**2021**) 102607. **IF=3.383**
6. I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, Low temperature X-ray absorption spectroscopy study of $CuMoO_4$ and $CuMo_{0.90}W_{0.10}O_4$ using reverse Monte-Carlo method, Rad. Phys. Chem. 175 (2020) 108411. **IF=2.858**
7. I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, Probing the Thermochromic Phase Transition in $CuMoO_4$ by EXAFS Spectroscopy, Phys. Status Solidi B 255 (2018) 1800074. **IF=1.71**
8. G. Bakradze, A. Kalinko, A. Kuzmin, X-ray absorption and Raman spectroscopy studies of tungstates solid solutions $Zn_cNi_{1-c}WO_4$ (c=0.0-1.0), Low Temp. Phys. 46 (2020) 1412. **IF=0.923**
9. I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, X-ray absorption near edge spectroscopy of thermochromic phase transition in $CuMoO_4$, Low Temp. Phys. 44 (2018) 434. **IF=0.923**
10. I. Pudza, A. Kuzmin, Treatment of disorder effects in X-ray absorption spectra by reverse Monte Carlo simulations: $CuMoO_4$ case, Acta Crystallogr. A 77 (**2021**) C602. **IF= 2.290**

EXPERIMENT + THEORY

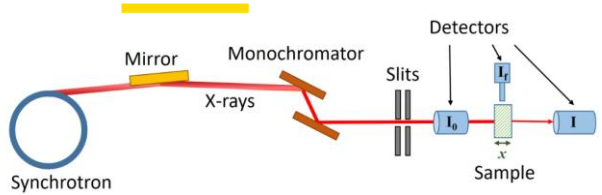
X-ray absorption spectroscopy (XAS) and **resonance X-ray emission spectroscopy** (RXES) were performed at the **PETRA-III** (DESY, Hamburg) and **ELETTRA** (Trieste) synchrotron centers.

These measurements were supplemented with X-ray photoelectron spectroscopy, Raman spectroscopy and X-ray diffraction measurements performed at the Institute of Solid State Physics of the University of Latvia, using the research infrastructure developed within the CAMART^2 project.

Theoretical methods such as the **multiple-scattering theory** and the **reverse Monte Carlo method** were used to interpret the experimental data.

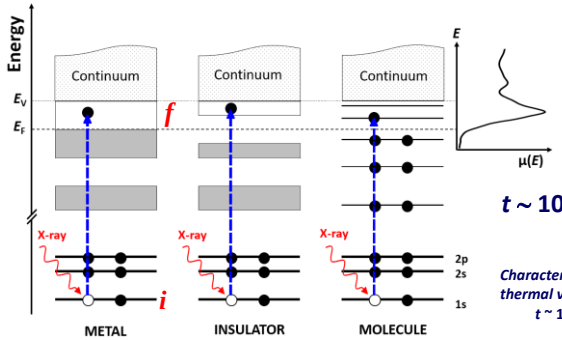


X-RAY ABSORPTION SPECTROSCOPY (XAS)



$$\mu(E) = \frac{1}{x}\ln\left(\frac{I_0(E)}{I(E)}\right)$$

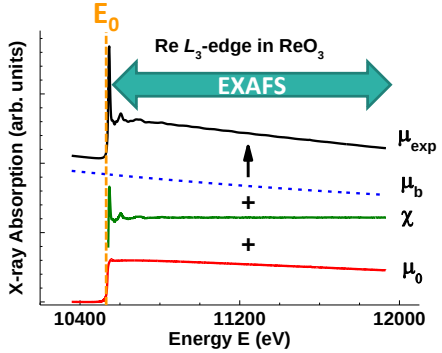
$$\mu(E) \propto \frac{I_{\text{fluo}}(E)}{I_0(E)}$$



$t \sim 10^{-15}$-10^{-16} s

Characteristic time of thermal vibrations: $t \sim 10^{-13}$-10^{-14} s

Separation of the Re L_3-edge X-ray absorption spectrum $\mu(E)$ of crystalline ReO_3 into three contributions due to the background $\mu_b(E)$, the EXAFS oscillations $\chi(E)$ and the atomic absorption $\mu_0(E)$.



$$\chi(k) = \frac{\mu(E) - \mu_b(E) - \mu_0(E)}{\mu_0(E)}$$

$$k = \sqrt{\frac{2m_e}{\hbar^2}(E - E_0)}$$

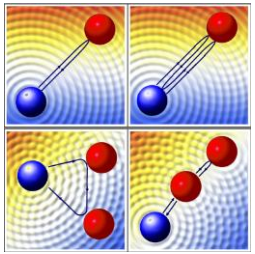
Fermi's Golden Rule

$$\mu(E) \propto \left|\langle f|\hat{H}|i\rangle\right|^2 \rho(E_f) = \mu_0(E)[1 + \chi(E)]$$

$$|f\rangle = |f_0\rangle + |\Delta f\rangle$$

$$\chi(E) \propto \langle \Delta f|\hat{H}|i\rangle \quad \Leftarrow \textbf{EXAFS}$$

Multiple-scattering (MS) expansion:

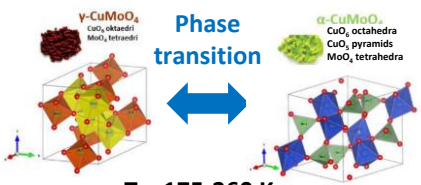


$$\chi(k) = \sum_{n=2}^{\infty} \chi_n(k),$$

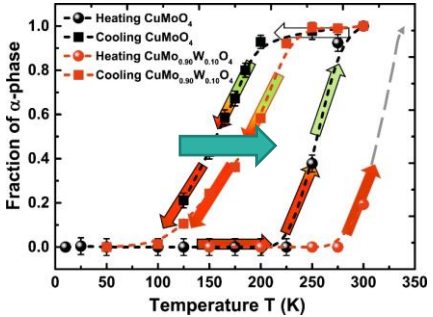
$$\chi_n(k) = \sum_i A_n^l(k, R_i)\sin\left(2kR_i + \phi(k, R)\right)$$

$$\boldsymbol{\chi_{CA}}(k) = \langle \chi(k) \rangle \quad \Leftarrow$$ **Configuration-averaged EXAFS (from MD or RMC)**

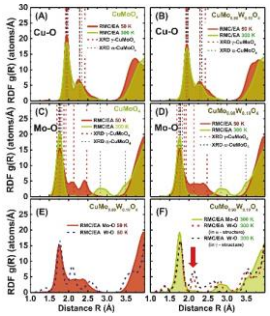
RESULTS (I): LOW-T



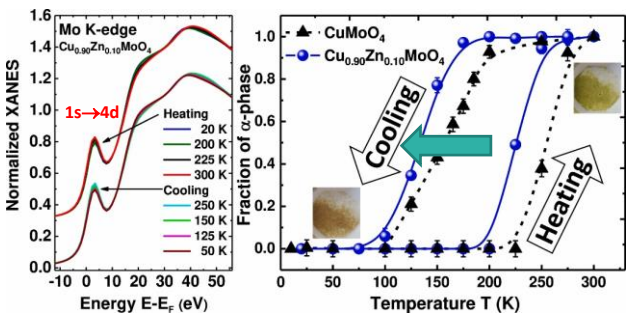
For the first time, we obtained detailed information on the local atomic structure of copper molybdate ($CuMoO_4$) and its solid solutions ($CuMo_{1-x}W_xO_4$, $Cu_{1-x}Zn_xMoO_4$). The obtained results allowed us to explain the thermochromic properties of these materials in both **low** (< –70°C) and high (> +100°C) temperature ranges, opening the possibility to create a temperature indicator/sensor in the desired temperature range.



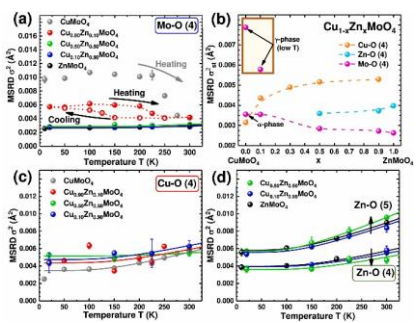
Tailoring of hysteresis loop



Local structure distortions from RMC



Tailoring of hysteresis loop



Tailoring properties

1. I. Pudza, A. Anspoks, A. Cintins, A. Kalinko, E. Welter, A. Kuzmin, The influence of Zn^{2+} ions on the local structure and thermochromic properties of $Cu_{1-x}Zn_xMoO_4$ solid solutions, Mater. Today Commun. 28 (2021) 102607. **IF=3.383**
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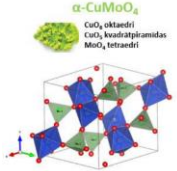
RESULTS (II): HIGH-T

No phase transition!



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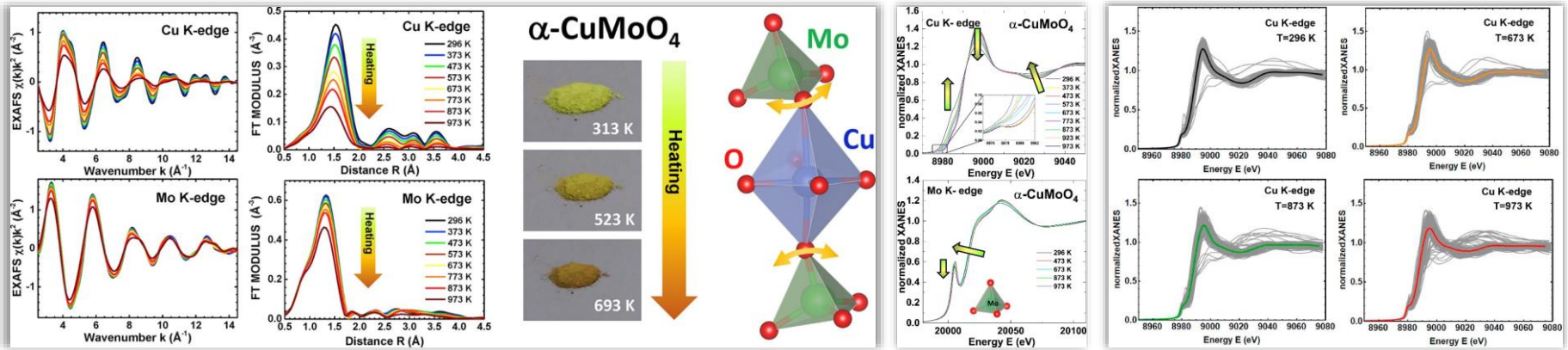


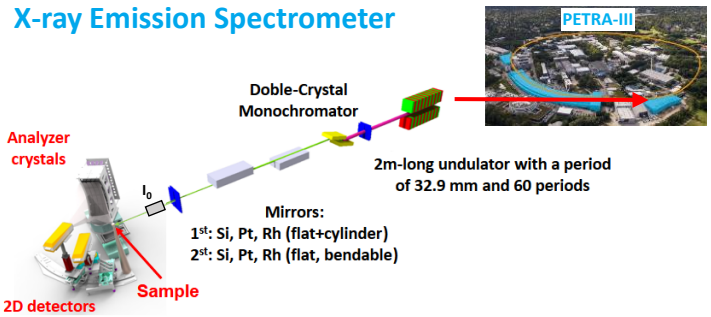
Dynamic nature of the $O^{2+} \rightarrow Cu^{2+}(3d^9)$ charge transfer band gap

1. I.Jonane, A. Anspoks, G. Aquilanti, A. Kuzmin, High-temperature X-ray absorption spectroscopy study of thermochromic copper molybdate, ***Acta Mater***. 179 (2019) 26. **IF=8.203**

RESONANCE X-RAY EMISSION SPECTROSCOPY (RXES) ≡ RIXS

$\Gamma_{\text{core-hole}}(3d_{5/2}) \approx 2.01$ eV $< \Gamma_{\text{core-hole}}(2p_{3/2}) \approx 4.57$ eV

High-Energy Resolution von-Hamos X-ray Emission Spectrometer



***A. Kalinko**, W. A. Caliebe, R. Schoch, M. Bauer, J. Synchrotron Rad. 27 (2020) 31-36.*

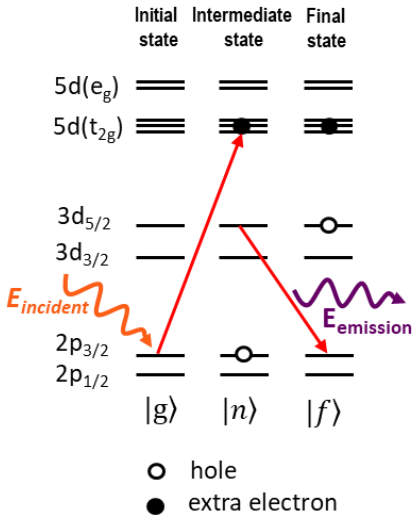
Spectrometer specifications

- Incident energy: **4.5 – 40 keV**
- Emission energy: **4.5 – 20 keV**
- Dispersion: **20 – 300 eV**
- Resolution: **0.15 – 1 eV**
- Bragg angles: **50° – 82°**

Analyzer crystals

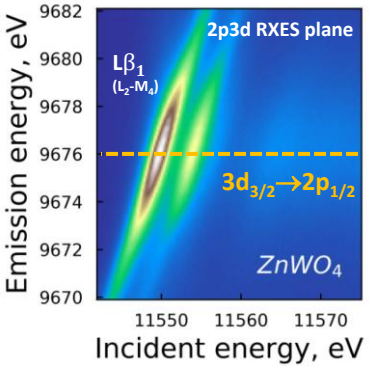
- 300µm **Si(311)**
- 6 crystals simultaneously

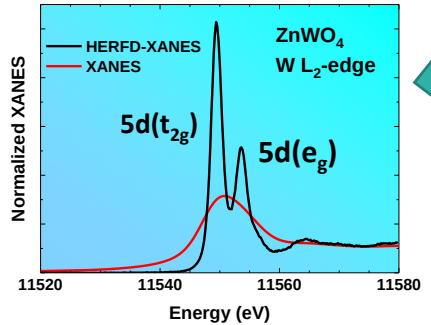
230×100 µm focused beam



2p3d RXES experiment

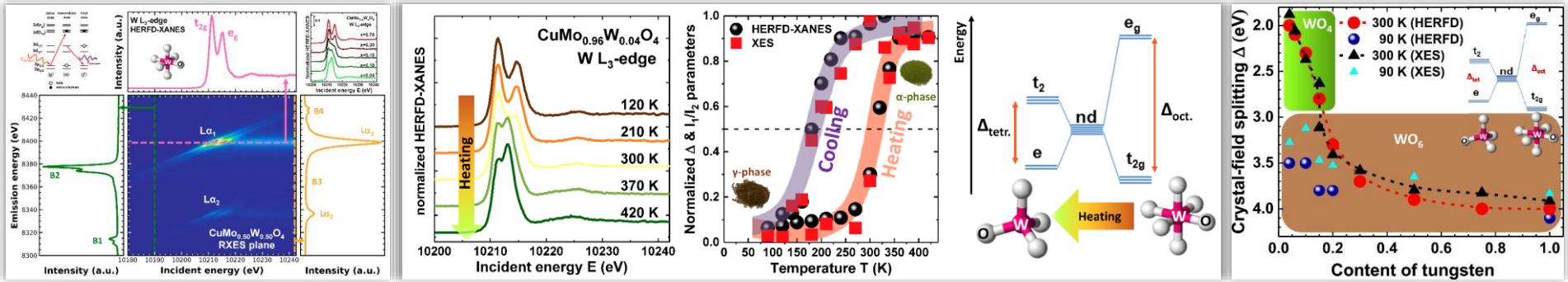
$$\mu(E) \propto \frac{I_{\text{fluo}}(E)}{I_0(E)}$$





RESULTS (III): CRYSTAL FIELD SPLITTING

A new approach to obtain information on the local deformations caused by the crystalline field has been demonstrated using the resonance X-ray emission spectroscopy at the **W L_3-edge**.



Type and magnitude of the crystal field splitting Δ can be determined by HERFD-XAS and off-resonant RXES

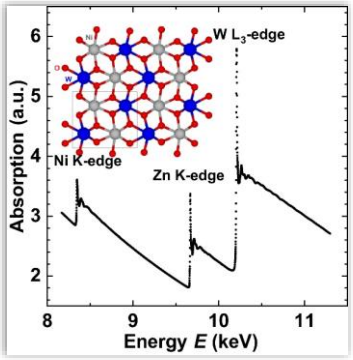
1. I. Pudza, A. Kalinko, A. Cintins, A. Kuzmin, Study of the thermochromic phase transition in $CuMo_{1-x}W_xO_4$ solid solutions at the W L_3-edge by resonant X-ray emission spectroscopy, ***Acta Mater***. 205 (2021) 116581. **IF=8.203**

RESULTS (IV): MAGNETIC DIMERS FROM EXAFS+RMC

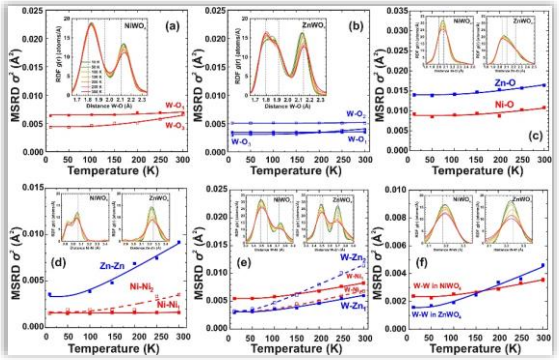
Exotic magnetic structures - **magnetic Ni^{2+} dimers** - have been **discovered** in **monoclinic** nickel tungstate ($NiWO_4$) and its solid solutions ($Zn_xNi_{1-x}WO_4$), which determine the magnetic properties of these materials (T_N=67 K for bulk $NiWO_4$).

A fundamental understanding of magnetic dimers may contribute to the field of spintronics in the future.

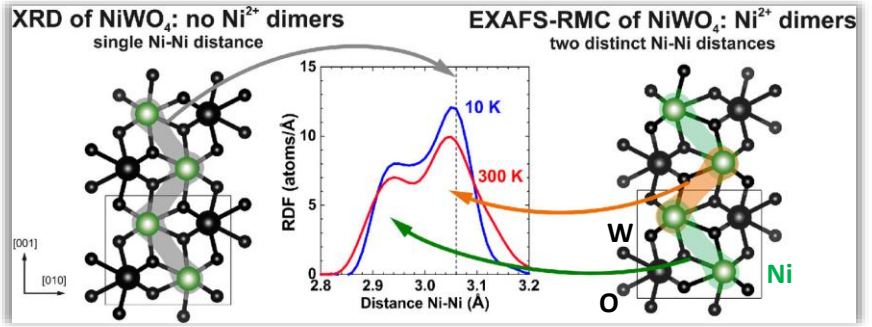
Such effect is known in **triclinic** $CuWO_4$ (1996-2001) but is absent in **monoclinic** $CoWO_4$ (2016).



Exceptional data



Structure + dynamics by RMC



Evidence for dynamic dimerization due to superexchange Ni^{2+} –O^{2-}–Ni^{2+} and the double-well potential along [001] direction (±0.02 Å)

1. G. Bakradze, A. Kalinko, A. Kuzmin, Evidence of dimerization of nickel ions in $NiWO_4$ and $Zn_cNi_{1-c}WO_4$ solid solutions probed by EXAFS spectroscopy and reverse Monte Carlo simulations, ***Acta Mater***. 217 (2021) 117171. **IF=8.203**

SUMMARY

Knowledge of the structure of a material and its dependence on external conditions and composition is important to understand and control the functionality of the material, which ultimately determines its practical applications.

In this work, we have performed a **systematic study** of a wide group of **smart materials** as **molybdates** and **tungstates**, whose functional properties are closely related to their **local atomic structure** and **chemical composition**.

Using **synchrotron radiation** sources and **high-performance computer modeling**,

- the relationship between the local structure distortion and lattice dynamics of **molybdates** and their **thermochromic properties** was **revealed** and **explained**.
- The presence of **magnetic dimers** was **discovered** in **tungstates** with high nickel content.

The obtained **results demonstrate new possibilities for the use of X-ray absorption spectroscopy** for accurate studies of the structure of functional materials, as well as help to understand the mechanisms of the thermochromic effects, which opens the way for practical applications.

FUNDING

The research was funded within 4 projects:

1. LZP projekts LZP-2019/1-0071 “Organisku-neorganisku hibrīdsistēmu izstrāde rentgenstarojuma detektēšanai” (2020-2022) (A. Kalinko).
2. PostDoc Latvija ERAF projekts Nr.1.1.1.2/VIAA/3/19/444 (2020-2022) (G. Bakradze).
3. SIA “Mikrotīkls” stipendija par darbu "Funkcionālo materiālu eksperimentālie un teorētiskie pētījumi sensoru pielietojumiem" (2017-2020) (I. Pudža).
4. L'ORÉAL-UNESCO Baltic Prize "For Women in Science" (2021) (I. Pudža).

FLPP
FUNDAMENTAL AND APPLIED RESEARCH PROJECTS

For Women in Science
FONDATION L'ORÉAL

MikroTik

PostDoc Latvia

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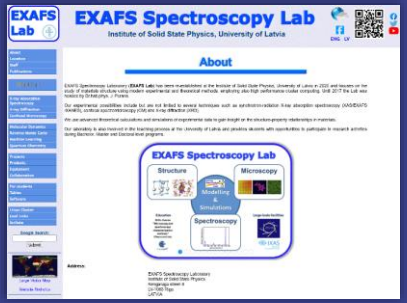

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