



Session VIII, May 28, Thursday

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VLIV URYCHLOVACÍHO NAPĚTÍ NA RTG LAMPĚ NA KVALITU DIFRAKČNÍHO ZÁZNAMU

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Rentgenové lampy používané v rámci strukturálních a mineralogických analýz lze provozovat v širokém spektru jejich volt – ampérové charakteristiky. Nejčastější

nastavení provozních parametrů bývá napětí 40kV a proud 30 mA. Přednáška bude prezentovat, jak mohou být některé z nastavení pracovního bodu RTG lampy ošidné.

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ROLE OF X-RAY DIFFRACTION IN INVESTIGATING STRUCTURAL PROPERTIES OF FUNCTIONAL MATERIALS

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X-ray diffraction (XRD) is one of the most effective and accessible methods for studying the structure of functional semiconductor materials, especially when defects and internal distortions play an important role. Its capabilities were illustrated for $Zn_{1-x}Mn_xTe$ thin films with 5 pct. Mn content, where the addition of alloying element introduces structural disorder. High-resolution XRD data were analyzed using a modified Williamson–Hall (W–H) approach, which makes it possible to distinguish between the effects of crystallite size and lattice strain while also considering directional (anisotropic) broadening caused by defects. The results show that peak broadening is mainly governed by strain (microstrain $\sim 10^{-3}$), while the crystallite size remains relatively large (>100 nm). The analysis also reveals dislocation densities on the order of $\sim 10^{14}$ – 10^{15} m⁻², increasing with Mn content, indicating a higher level of structural defects. The films exhibit a preferred (111) ori-

entation, and pole figures confirms partial strain relaxation and slight crystal misorientation (tilt of a few tenths of a degree). When combined with complementary techniques such as SEM and HRTEM, XRD method enables a more complete and consistent understanding of structural properties across different length scales. This makes it a key tool for understanding how material structure influences the performance of functional thin films in applications such as optoelectronics and spintronics.

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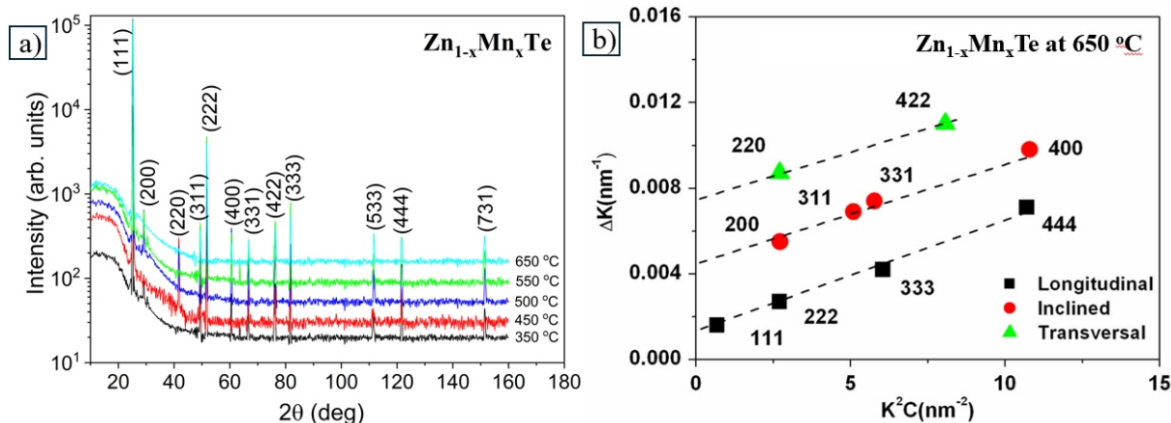


Figure 1. (a) X-ray Diffraction patterns of $Zn_{1-x}Mn_xTe$ films with a nominal Mn content of 5%, deposited on glass substrates by close-space vacuum sublimation (CSVS) at different substrate temperatures; (b) modified Williamson–Hall plot of the $Zn_{1-x}Mn_xTe$ film grown at 650 °C.

1. Martinez-Tomas, C., Klymov, O., Agouram, S. *et al.*, “Substructural Properties and Anisotropic Peak Broadening in $Zn_{1-x}Mn_xTe$ Films Determined by a Combined Methodology Based on SEM, HRTEM, XRD, and HRXRD”, *Metall Mater Trans A* **47**, 6645–6654 (2016).
2. T Ungár, “Microstructural parameters from X-ray diffraction peak broadening”, *Scripta Materialia*, **51** (8), pp. 777-781 (2004).
3. Fewster, P. F., *X-ray Scattering from Semiconductors*, London, U.K.: Imperial College Press, (2003)

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BENTONITE RESEARCH FOR CZECH DEEP GEOLOGICAL REPOSITORY OF NUCLEAR WASTE: WHAT DOES XRD TELL US?

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Bentonite is an absorbing swelling clay material consisting mainly of minerals from a smectite group. Smectites are expandable aluminium phyllosilicate minerals, with very small crystallites and large surface area. This property makes them excellent adsorbent. Therefore, bentonites are considered to be the most suitable materials for the multibarrier system of a deep geological repository (DGR) of high-level radioactive waste. Most concepts of DGR consider temperatures up to 100 °C. An increase in temperature could lead to cost savings due to increasing disposal capacity. The relevant mineralogical research on bentonite material at 200 °C has been performed to clarify mineralogical and geochemical changes that occur during heating. Pelletized bentonite extracted from Černý vrch deposit (BCV) and processed at Keramost Ltd. Obrnice Plant (Most, Czech Republic) was used as a tested material. The BCV material represents Czech Mg-Ca bentonite and consists of mainly of montmorillonite, minority of kaolinite, quartz, illite, Mg-calcite, goethite and traces of other carbonates including siderite and ankerite.

The conducted research consists of two parts. The first part investigates the effect of long-term thermal loading up to 200 °C on the properties of the bentonite barrier within a mock-up in-situ experiment conducted in the Josef Underground Research Laboratory (Figure 1), Smilovice-

Chotilsko, ČR. The results provide insight into the changes occurring in the bentonite as a function of the distance from the heater and contribute to the assessment of the stability of Ca–Mg type bentonite under elevated temperature conditions in the initial period of the lifetime of the DGR. The second part presents a complementary laboratory programme and summarizes the results of the study of BCV bentonite subjected to thermal loading at 200 °C under dry conditions. These laboratory experiments simulate a worst-case thermal scenario (200 °C), associated with intensive drying of the bentonite in the vicinity of the disposal canister shortly after its emplacement in a deep geological repository for high-level radioactive waste.

Powder X-ray diffraction was applied for monitoring the mineralogical composition of studied bentonite. XRD was also used in determination of the layer charge of smectite. Permanent layer charge is an important intrinsic property of smectites which stems in general from cation substitutions in the octahedral and/or tetrahedral sheet or from vacancies in the octahedral sheet. The procedure involving Cu-triethylenetetramine complex (Cu-Trien) exchange followed by ethylene glycol (EG) solvation, registered via XRD was used primarily for distinguishing the layer charge. The laboratory experiments confirmed a decrease in cation exchange capacity and a reduction in the

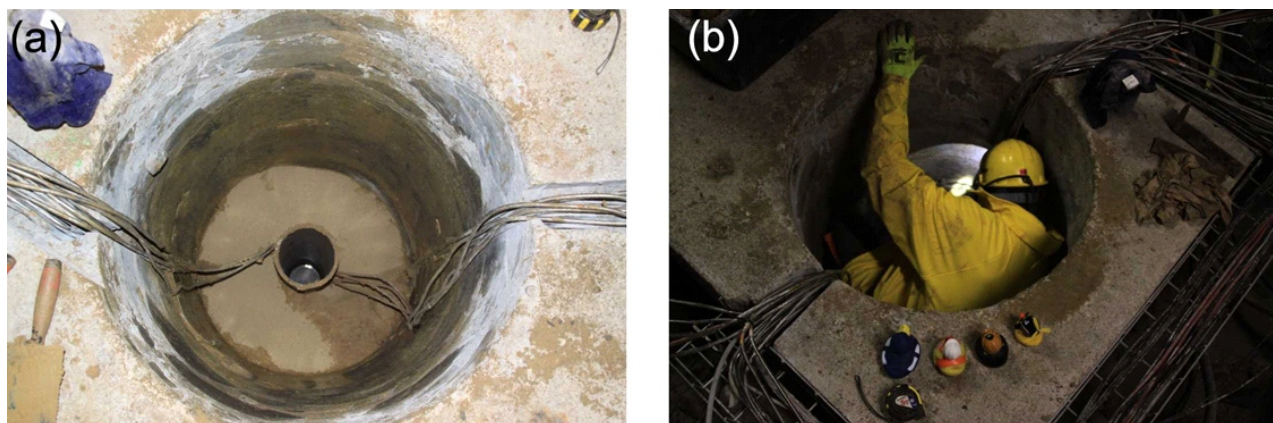


Figure 1. (a) Bentonite barrier within a mock-up in-situ experiment conducted in the Josef Underground Research Laboratory during dismantling of the experiment. The heating housing tube is visible in the centre. (b) Sampling of bentonite samples for mineralogical analysis with the dismantling procedure.



average layer charge of smectite as a result of Mg^{2+} fixation [2]. Subsequent rehydration tests demonstrated only partial reversibility of these changes. Mineralogical and geochemical analyses of samples collected during the dismantling of the experiment demonstrated that the thermal impact on the

bentonite is spatially limited to a narrow zone in the immediate vicinity of the heater.

1. M. Koubová, P. Vorm, J. Lang, O. Petrov, *Appl. Clay Sci.*, **232**, (2023), 106788.
2. M. Koubová, F. Laufek, I. Hanusová, M. Szczerba, *Appl. Clay Sci.*, **270**, (2025), 107773.

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BORON CAGES IN MOF

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Crystallographic techniques are powerful tools for determining the structure and spatial arrangement of atoms and molecules in crystalline materials. However, not all molecules form well-ordered crystals. In cases where high precision methods such as X-ray or electron diffraction do not provide sufficient structural detail, force field based molecular dynamic simulations can offer valuable insights into the positions and behavior of individual molecules within Metal-Organic Frameworks (MOF).

Applying molecular dynamics to MOF structures containing boron-18 clusters and cyclohexane molecules can significantly accelerate the process of crystal structure determination. This approach allows for a more detailed understanding of anchoring sites and intermolecular interactions within the frameworks.

The first phase of calculations focuses on the preparation of MOFs and their detailed characterization, particularly in terms of crystallinity and number of defects (expressed as the ligand-to-metal ratio). The study begins with the well-established prototypical Fujita MOF

$[(ZnI_2)_3(\text{tpt})_2], [1]$ where tpt denotes 2,4,6-tris(4-pyridyl)-1,3,5-triazine. This MOF serves as a host structure for the adsorption of non-polar molecules such as cyclohexane and boron clusters.

Using this model system with stable boron 18 cages, we will investigate the potential and limitations of combining molecular dynamics simulations with single crystal X-ray diffraction to improve the precision of structural determination.

1. Y. Inokuma, et al. *Nature*, **495**, (2013), 461-466.
doi.org/10.1038/nature11990

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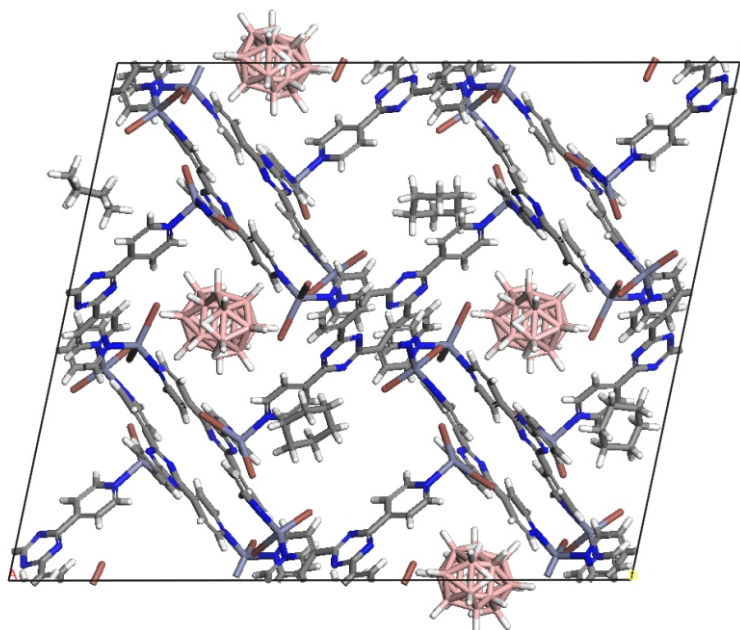


Figure 1. Z-view of MOF structure with boron (B18) cages and cyclohexane molecules from quench molecular dynamics in NVT ensemble, $T = 298$ K, timestep 1 fs, Nose thermostat.

NEW MATERIAL AND TECHNOLOGICAL ASPECTS OF ANCIENT RED-FIGURE POTTERY FROM SOUTHERN ITALY

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Red-figure is one of the main types of pottery decoration used by ancient Greeks introduced in ancient Athens around 530 BCE. In this technique, the background is painted black while the figures and other depicted objects or ornaments use the natural colour of the clay. The distinctive colour of the black gloss was achieved through the presence of magnetite (Fe_3O_4), while the lustrous appearance resulted from a partially vitrified clay-based matrix. The black slip stands in sharp contrast to the light clay body, whose colour ranges from yellow to red depending on the iron content in the form of hematite (Fe_2O_3). The highest quality pottery was produced in Athens, where the local clay is naturally rich in iron, resulting in a deep black slip and an intense red clay body. In the 5th century BCE, red-figure pottery was exported to other parts of the Greek world, such as southern Italy where local production centres arose. The transmission of both the red-figure and black gloss techniques still raises many questions regarding the origin and training of the first artisans, their adaptation to local resources, and the interaction between newly introduced and Indigenous techniques. [1]

To understand painting technique and identify possible divergence from the original Attic production, eleven red-figure objects from the collection of the Faculty of Arts, Charles University in Prague, dated to the second half of the 4th century and produced in Apulian, Campanian and Lucanian workshops, were studied non-invasively using hand-held X-ray fluorescence (XRF), X-ray powder diffraction (XRPD), infrared (FTIR) and Raman spectroscopy and optical microscopy (OM) (Fig. 1, 2). In addition, scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) and small angle neutron scattering (SANS) were used for investigation of fragmentary pieces.

The comprehensive study of these ancient vases demonstrates that the black gloss technology diverges in certain aspects from the traditional procedures used in mainland Greece. The most striking differences were the presence of low-temperature phases, such as clay minerals, gypsum, and calcium oxalates in the form of whewellite or weddellite. Oxalates and gypsum in the black gloss and clay body were interpreted as secondary (degradation) products resulting from microbial activity and sulphate-rich environment usual for funeral sites near gypsum-bearing rock formations. On the other hand, the clay minerals, part of the original material, are present in differ-



Figure 1. The XRPD analysis of Plate 26.3 (4th century BCE, Apulia, South Italy). Photo P. Bezdička.

ent forms: in the black gloss in a dehydroxylated state, and the clay body with structurally bound hydroxyl groups. This finding implies that the clay body was fired under milder conditions than the black gloss, or that the firing duration was too short to fully heat the thick clay body, resulting in the retention of the clay minerals in this form.

Another striking difference is the absence of magnetite in the black gloss of some vases, where it is replaced either by hercynite or other spinel phases (typically found alongside magnetite), or by carbon black. The presence of spinel phases generally contrasts with the mild firing temperatures indicated by the presence of clay minerals. This suggests a new technique for producing spinel-based black slip, in which the spinel phases were prepared in advance and mixed with a clay-based filler material. This slip was applied to the vase, and the entire piece was fired under mild conditions. The firing process may also have been significantly shorter. This new technique indicates a tendency toward more economical production of red-figure pottery. The separately manufactured spinel-based material (or even its complete substitution by carbon black) could be produced in larger quantities and extended with filler material. Firing the entire painted piece quickly, low-temperature would also have been inexpensive compared to the traditional three-phase firing cycle. [2]

1. A. D. Trendall, *Red Figure Vases of South Italy and Sicily: Handbook*, London. 1989, pp. 288.

