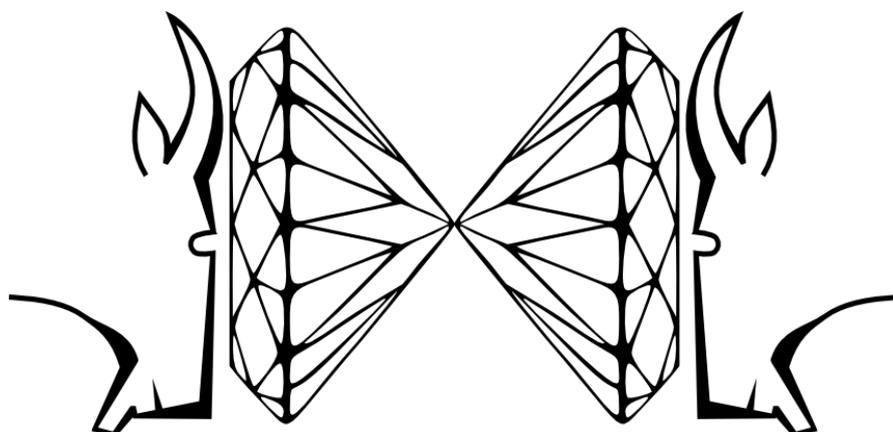


**6TH FROLIC GOATS
WORKSHOP ON HIGH
PRESSURE DIFFRACTION**

Abstract Book

Poznań, 14-16 April 2013



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Welcoming address

The Frolic Goats Workshop on High-Pressure Diffractometry continues the mission of disseminating the general knowledge about the application of varied thermodynamical conditions in crystal chemistry, physics and biology. Of various thermodynamical conditions for many years pressure remained most complicated experimentally and most expensive for diffraction measurements. However, after the advent of diamond-anvil cell (DAC) and all concurrent inventions in x-ray diffractometry, and particularly the 2-dimensional detectors, passports to the realm of high-pressure have become cheaper and easier accessible. Of the scientific community the crystallographers are most privileged, as they have the command of x-ray diffractometers and they understand transformations of crystal structures. Here we wish to give into their hands the most powerful tool for modifying crystal environment. For nearly three decades it has been our aim to facilitate high-pressure diffraction experiments. They consist of several stages, involving the handling and alignment of the DAC, its loading, pressure calibration and running the diffractometer measurement, which are specific to high-pressure experiments. Therefore we decided to organize this workshop, where the high-pressure techniques could be explained and practiced. Hence, apart from theoretical lectures, the specific tasks of handling the DAC can be performed together with experienced colleagues. But most importantly, it was our intention to create a forum of high-pressure scientists for direct exchange of experience, views and other contacts.

Traditionally, the Workshop includes a social event, for establishing informal ties between the participants. This year, despite thick layer of snow in April, we will cycle to the Morasko Meteorite Reserve, to see craters left after a rain of meteorites fell there some 5000 years ago. We will also see the meteorite, of about 200 kg and the largest in this part of Europe, found at that site recently.

This is the first Frolic Goats Workshop to be held partly in the Morasko Campus in the new Collegium Chemicum building, as the Faculty of Chemistry is in the process of moving from the old premises in Grunwaldzka Street – the diffractometers and other equipment are still located there and hence all the practical exercises on Tuesday will be held in the old building in the city centre.

Finally, it is my pleasure to thank all the sponsors of the Workshop, the Faculty of Chemistry, Agilent and Bruker Polska for financial support, as well as the CrystEngComm journal of the Royal Society of Chemistry for funding two book awards for the best posters.

I also thank all the members of the Organizing Committee and all teachers in the Workshop for their efforts.

Wishing you the fruitful sessions,

Andrzej Katrusiak

Scientific programme

Sunday, 14 April 2013

14⁰⁰ *Bicycle trip to the Morasko Meteorite Nature Reserve. After returning to Collegium Chemicum in the Morasko Campus, a get-together barbeque in the backyard square between blocks A and B*

Monday, 15 April 2013

8³⁰ *Registration, room 2.57 Collegium Chemicum, Morasko Campus*

9⁰⁰ A. Katrusiak *Opening ceremony*

9⁰⁵ A. Katrusiak *Strain in materials*

9³⁵ M. Hanfland *Single crystal diffraction at the ID09A beamline of the ESRF*

10³⁰ M. Stachowicz *High Pressure Achievements in Warsaw. Conducting materials*

10⁴⁵ M. Anioła *Pressure-induced conformational phase transition in 4,4'-bipyridine hydro-bromide monohydrate*

11⁰⁰ W. Cai *High-pressure Crystallization of DL-Mandelic Acid Racemate*

11¹⁵ K. F. Dziubek *High Pressure Diffraction Study of Toluene Pursued in a Collaborative Project*

11³⁰ *Coffee break*

12⁰⁰ M. Bujak *Low-temperature and high-pressure behaviour of 1,2,4-trichlorobenzene. Melting point differences in trichlorobenzene isomers*

12³⁰ M. Daszkiewicz *Comparative studies of 2-methyl-4-nitroanilinium hexachlorido-stannate(IV), bromide and two non-centrosymmetric chlorides*

13⁰⁰ M. Meyer *HP experiments and data reduction with CrysAlisPro*

14⁰⁰ *Poster session and poster awards*

16⁰⁰ *Visit to the Meteorite Exhibition in the Faculty of Geology 1.5 km from Collegium Chemicum - participants should meet at the stairs to Collegium Chemicum at 15⁴⁰*

Tuesday, 16 April 2013

9³⁰ *Laboratory exercises: DAC construction, alignment, loading, diffraction experiment – room 24, old Collegium Chemicum, Grunwaldzka Street.*

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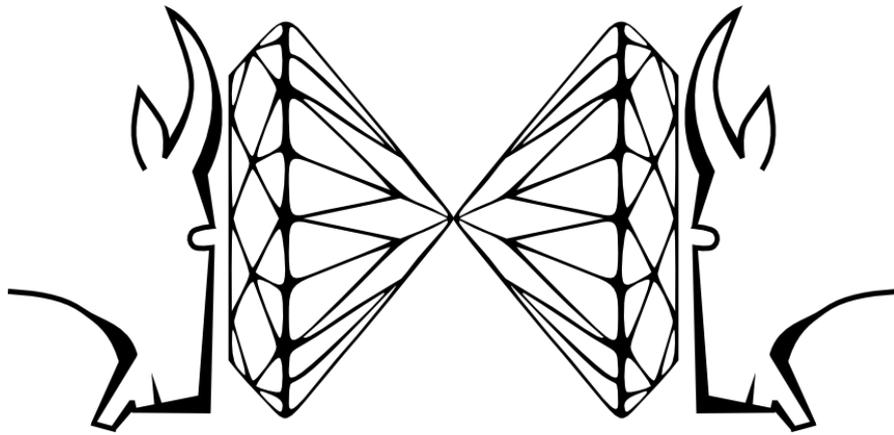
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Lectures

Strain in materials

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Materials transform at varied thermodynamic conditions. The most commonly considered thermodynamic parameters are temperature, T , pressure, p , and chemical composition, d . The changes of materials properties as the function of these parameters are often investigated and the size and shape changes of this material is described as its strain. Materials can be generally classified as isotropic and anisotropic, and their transformations as monotonic and anomalous. For small monotonic changes in hydrostatic pressure, p , temperature, T , and homogenous composition changes (e.g. chemical doping, d), which can be considered as generalized isotropic stress F , changes in isotropic materials between their equilibrium states result in isotropic strain S , described by the linear relation:

$$S = c \cdot F \quad (1),$$

where c is a scalar. For a small stress, σ , Equation 1 is the classical Hook's law:

$$\Delta l = \beta_l \cdot \sigma \quad (2),$$

where Δl is the length change, and β_l is the linear compressibility coefficient. Similarly, materials deform for small temperature changes:

$$\Delta l = \alpha_l \cdot T \quad (3),$$

where α_l is the linear thermal expansion coefficient, and an analogical relation with parameter γ_l can be defined for small chemical changes.

For describing the strain in anisotropic materials and anisotropic stress, σ_{kl} , the tensor relation of generalized Hook's law must be applied:

$$S_{ij} = c_{ijkl} \cdot \sigma_{kl} \quad (4),$$

involving the 2nd rank strain, 4th rank elastic and 2nd rank stress tensors, respectively.

The algebraic and geometric representation of this interdependence will be presented for different symmetry and compressibility magnitudes.

References

- [1] J. F. Nye, *Physical Properties of Crystals*, Oxford at the Clarendon Press 1957.
- [2] L. D. Landau & J. M. Lifszyc, *Teoria sprężystości [Theory of Elasticity, in Polish]*, Wydawnictwo Naukowe PWN, Warsaw 2008.

Single crystal diffraction at the ID09A beamline of the ESRF

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ID09A uses monochromatic diffraction with large area detectors. Structural studies on powdered samples or single crystals can be performed at high pressures in diamond anvil cells. It provides beam sizes down to 10 x 10 μm to study samples from a few GPa to approximately 200 GPa at 30 keV and very high photon fluxes. It offers state of the art optical systems for additional in situ characterization of the samples at high pressure and a highly developed sample environment.

Recent technical advances have significantly added to the utility of single crystal X-ray diffraction experiments at high pressures. New ways of supporting diamond anvils, like Boehler Almax anvils [1], have considerably increased the volume of accessible reciprocal space. Use of Helium as pressure transmitting medium extends substantially the practicable pressure range. Flat panel detectors have noticeably decreased the data collection time and increased the accuracy. Data can be collected at low and high temperatures. Even single crystal diffraction experiments with laser heating have become possible [2]. Here we will present several examples to illustrate the recent progress.

References

- [1] R. Boehler, K. DeHantsetters, *High Press. Research* **24** (2004) 391.
- [2] I. Kuzenko et al., *Rev. Sci. Instrum.* **83** (2012) 124501.

High Pressure Achievements in Warsaw. Conducting materials

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There have been much attention given to the construction of the new conducting materials composed of the segregated stacks of typical electron-donating (TTF, ET) and electro-accepting molecules (TCNQ, TCNE) – so called charge transfer complexes. It is crucial to investigate the properties of such systems at the electronic level in order to understand the nature of these complexes.

The following project concerns the clarification of the role of the $\pi\cdots\pi$ interactions on the structure and electronic properties of charge transfer complexes incorporating the macrocyclic complexes (electron donor) and the electron-deficient molecules. Three model macrocyclic complexes 14Ni, 14Cu i 14Pd have already been cocrystallized with the TCNQ molecule (see Fig 1.). In the crystal lattice these complexes create homo and hetero-molecular stacks of molecules interacting with each other via $\pi\cdots\pi$ interactions. We plan further crystallizations of these model macrocyclic complexes with other possible electro-deficient systems (TCNE, F4-TCNQ) We also conducted the high pressure experiments for one of these co-crystals. Under pressure of 0.40 GPa the separation between the Ni atom and the centroid of the TCNQ ring is decreased from 3.899 Å to 3.875 Å. We plan further high pressure X-Ray measurements for this system.

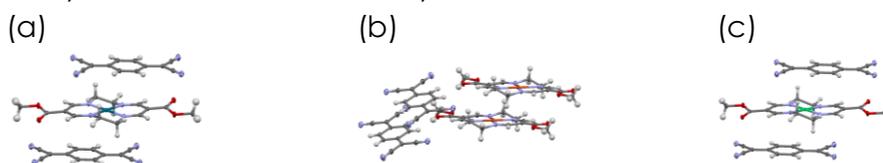


Fig. 1. Packing pattern of cocrystal (a) 14Pd with TCNQ, (b) 14Cu with TCNQ, (c) 14Ni with TCNQ.

The second part of our project is focused on superconducting materials (II type). We cooperate with the Institute of Physics, Polish Academy of Science studying FeTe_xSe_{1-x} single crystals of varying composition. Among the Fe-based superconductors, the '11' system has attracted a lot of attention. Simple chemical formula, as well as a smaller toxicity than this of the arsenic compounds (which were earlier intensively studied), are the main reasons to consider Fe-Te-Se as a model system for investigation of the mechanism of superconductivity and relation between structural, magnetic, and superconducting properties in this family of compounds. Additionally the '11' system has the simplest crystallographic structure among the Fe-based superconductors. Samples are prepared by the Bridgman method. Up to now we have performed single crystal X-ray analysis of FeTe_{0.5}Se_{0.5} at various temperatures in the range from 10 up to 300K. We observed ca. 50% increase of transition temperature (to 16 K). For this reason we decided to study structural changes influenced by pressure in this compound. The experiment has been performed under the pressure of 1.2 GPa, on a single crystal, using the Merrill-Bassett diamond anvil cell. Further experiments under higher pressures are planned for this material.

Pressure-induced conformational phase transition in 4,4'-bipyridine hydrobromide monohydrate

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Phase α of 4,4'-bipyridine hydrobromide monohydrate, 4,4'-bpHBr·H₂O is orthorhombic, space group $P2_12_12_1$ and it can be compressed to 1.4 GPa at least. The high pressure β -phase requires recrystallization of the compound above 0.55 GPa. Phase β is monoclinic space group $P2_1/c$.

High-pressure experiments were performed in a modified Merrill-Bassett diamond-anvil cell (DAC) [1]. The ruby-fluorescence method and a Photon Control spectrometer [2] were used for calibrating pressure; accuracy of 0.02 GPa was obtained. X-Ray measurements were performed with a KUMA KM4-CCD diffractometer [3].

Phases α and β are isostructural in the arrangement of cations NH⁺···N bonded into chains parallel to ···HOH···Br··· bonded chains. In phase β the ···HOH···Br··· chains increase the frequency of their zigzag motifs, and the 4,4'-bpH⁺ cations change their conformation in phase α . The cations are twisted by about 30° in phase α and in phase β they assume an energy-unfavorable planar conformation.



Fig. 1 Structural formula of 4,4'-bpHBr·H₂O.

References

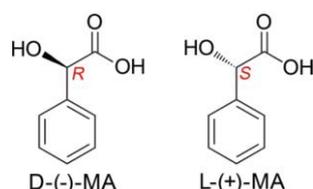
- [1] (a) L. Merrill, W. A. Bassett, *Rev. Sci. Instrum.* **45** (1974) 290; (b) A. Katrusiak, *Acta Crystallogr.*, **A64** (2008) 135.
- [2] H. K. Mao, J. Xu, P. M. Bell, *Geophys. Res.* **91** (1985) 4673.
- [3] A. Budzianowski, A. Katrusiak, in *High-Pressure Crystallography*, Kluwer Academic Publisher, Dordrecht, **140** (2004) 101.

High-pressure Crystallization of DL-Mandelic Acid Racemate

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Mandelic acid, $C_6H_5CHOHCOOH$, MA (Scheme 1), is one of frequent exempts from the Wallach's rule, as its racemate DL-MA is less dense than the enantiomers. This relation appears unfavourable for the racemate stability at high-pressure, however the racemate remains more stable than the conglomerate of enantiomers up to 1.36 GPa at least. The isochoric crystallization of DL-MA yields its orthorhombic form I, space group $Pbca$, and above 0.65 GPa another centrosymmetric polymorph of monoclinic DL-MA form II, space group $P2_1/c$, becomes stable [1]. Their structures have been determined by X-ray diffraction of the single crystals *in situ* grown in a diamond-anvil cell (DAC) up to 1.36 GPa (Figure 1). Lattice-energy calculations by the semiempirical PIXEL method demonstrate that DL-MA form II is more stable than DL-MA form I, and both these racemates are more stable than their enantiomer counterpart L-MA.



Scheme 1. Enantiomers of mandelic acid (MA)

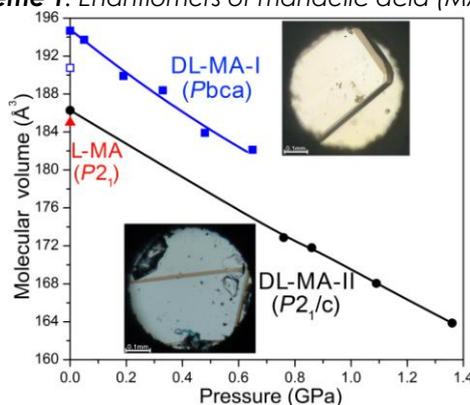


Figure 1. The molecular volume V_m (V/Z) of DL-MA in the function of pressure at 296 K for DL-MA-I (blue squares) and DL-MA-II (black circles). Also, the DL-MA at 0.1 MPa/150 K (blue open square) and L-MA (red triangle, ref 2) have been indicated. The insets show the crystal habits of DL-MA-I and II, as observed in the DAC.

This work was supported by TEAM Grant 2009-4/6 of the Foundation for Polish Science.



References

- [1] I. B. Rietveld, M. Barrio, J.-L. Tamarit, B. Do, R. Céolin, *J. Phys. Chem. B*, **115** (2011) 14698.
 [2] A. O. Patil, W. T. Pennington, I. C. Paul, D. Y. Curtin, C. E. Dykstra, *J. Am. Chem. Soc.*, **109**, (1987) 1529.

High Pressure Diffraction Study of Toluene Pursued in a Collaborative Project

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Last year we have decided to encourage the participants of the "Frolic Goats Workshops on High-Pressure Diffraction" (the event held at A. Mickiewicz University in Poznań annually since 2008 [1]) to work on a common task. Since we are coming from different places, equipped with various facilities (radiation sources, diffractometers, diamond anvil cells, computer software), the project assesses the reproducibility of high pressure single-crystal measurements and is a kind of round robin test evaluating the different procedures used to determine the crystal structure.

As a test sample we have chosen toluene, a common compound used in chemical laboratories. Toluene is known to crystallize at ambient pressure and low temperature in two different crystal forms: the stable monoclinic α polymorph, space group $P2_1/c$, $Z = 8$ [2], and the metastable orthorhombic β modification, space group $Pbcn$, $Z = 8$ [3]. The addition of the methyl group to the benzene ring perturbs the molecular arrangement found in benzene and introduces C-H $\cdots\pi$ interactions as the cohesive forces. High pressure investigation of toluene is particularly interesting in comparison with our former high pressure studies of benzene [4] and ethynylbenzene [5].

Two previously unknown high pressure polymorphs of toluene were discovered and their structure determined. Diffraction data were complemented with compression measurements performed in a piston-and-cylinder apparatus. Details of these findings will be presented at the workshop.

This work was supported by TEAM Grant 2009-4/6 of the Foundation for Polish Science.



References

- [1] <http://frolicgoats.amu.edu.pl>
- [2] S. K. Nayak, R. Sathishkumar, T. N. Guru Row, *CrystEngComm*, **12** (2010) 3112.
- [3] D. Andre, R. Fourme, J. Bruneaux-Pouille, L. Bosio, *J. Mol. Struct.*, **81** (1982) 253.
- [4] A. Katrusiak, M. Podsiadło, A. Budzianowski, *Cryst. Growth Des.*, **10** (2010) 3461.
- [5] K. F. Dziubek, M. Podsiadło, A. Katrusiak, *J. Am. Chem. Soc.*, **129** (2007) 12620.

Low-temperature and high-pressure behaviour of 1,2,4-trichlorobenzene. Melting point differences in trichlorobenzene isomers

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The high-pressure, supported by the low-temperature, X-ray diffraction is a powerful experimental method for studying molecular systems and their properties. The low-temperature and in particular high-pressure conditions can significantly alter the nature and hierarchy of inter- and intramolecular interactions and stabilities of molecular systems.

Halogenated benzenes could be considered as a group of model organic compounds for studying the molecular packing, the role played by intra- and intermolecular interactions together with the structure-property relations, such as density as well as the boiling and melting temperature and pressure. The most studies, using both experimental and theoretical methods, have been devoted to solid at ambient conditions compounds, in particular those showing polymorphism and phase transitions. The liquid compounds, because of the much more complicated experimental methodology as compared to the routine data collection procedures of solid samples, were much less investigated [1, 2].

Among trichlorobenzene C₆H₃Cl₃ isomers, only the low-symmetry (C_s) 1,2,4-trichlorobenzene is a liquid at ambient conditions. The molecular symmetry of remaining two 1,2,3- and 1,3,5-trichlorobenzenes is higher (C_{2v} and D_{3h}, respectively) and they are solids. The comparable boiling points and significantly different melting points clearly suggest differences between those isomers in their structures and intermolecular interactions. The presentation will be focused on the results of low-temperature and high-pressure structural investigations of 1,2,4-trichlorobenzene including its *in-situ* crystallization and single-crystal X-ray diffraction studies together with the structure-property relations to the remaining two 1,2,3- and 1,3,5-trichlorobenzene isomers [3].

References

- [1] D. Andre, R. Fourme, M. Renaud, *Acta Crystallogr.* **B27** (1971) 2371.
- [2] R. Boese, M. T. Kirchner, J. D. Dunitz, G. Filippini, A. Gavezzotti, *Helv. Chim. Acta*, **84** (2001) 1561.
- [3] M. Bujak, M. Podsiadło, A. Katrusiak, *CrystEngComm* (in preparation).

Comparative studies of 2-methyl-4-nitroanilinium hexachloridostannate(IV), bromide and two non-centrosymmetric chlorides

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The 2-methyl-4-nitroaniline (2m4na) is studied due to non-linear optical properties which are related to the non-centrosymmetric crystal structure studied both experimentally and theoretically [1-3]. Crystal structures of two polymorphs of [H2m4na]Cl ($1\alpha, 1\beta$) and (H2m4na)₂SnCl₆·H₂O (2), where 2m4na = 2-methyl-4-nitroaniline, are shown and comparison of these crystal structures with the bromide salt reported earlier is presented. In all the presented crystal structures, alternatively arranged cations and anions form chain and ring hydrogen bonding patterns of weak unconventional N–H···Cl hydrogen bonds. Interrelations among the elementary graph-set descriptors and descriptors of the hydrogen bonding patterns are presented. Non-hydrogen bonding interactions between the nitro groups are also described using graph-set descriptors. Comparison of the experimental, also for deuterated 1α polymorph, and theoretical, for H2m4na⁺ ion with B3LYP/6-31G(d,p), spectra showed good agreement among the frequencies due to very weak interactions existing in studied compounds. Detailed analysis of the spectra revealed that the interaction between adjacent –NO₂ groups in 1α is stronger than the other types involving the nitro group. The bands were assigned on the basis of theoretical calculations of vibrational frequencies for H2m4na⁺ ion and PED analysis.

References

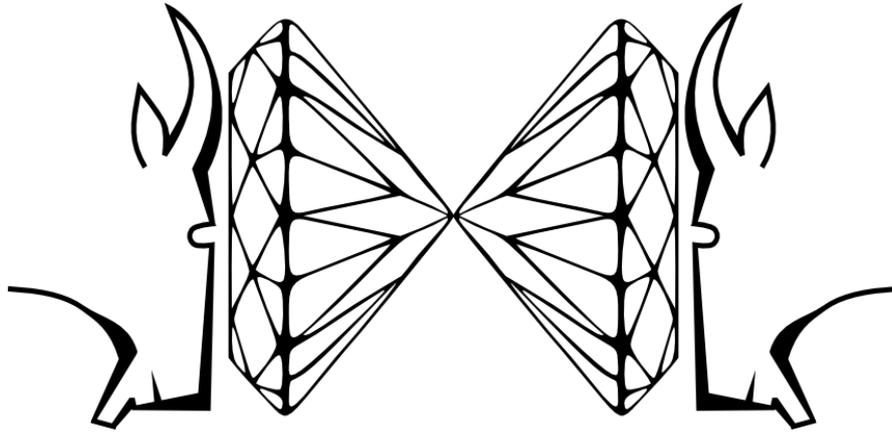
- [1] B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch, J. L. Bernstein, *J. Appl. Phys.*, **50** (1979) 2523.
- [2] A. E. Whitten, P. Turner, W. T. Klooster, R. O. Piltz, M. A. Spackman, *J. Phys. Chem., A* **110** (2006) 8763.
- [3] U. Okwieka, M. M. Szostak, T. Misiaszek, I. Turowska-Tyrk, I. Natkaniec, A. Pavlukojeć, *J. Raman Spectrosc.*, **39** (2008) 849.

HP experiments and data reduction with CrysAlisPro

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Version 171.36 of CrysAlisPro gives an extended support of HP experimentation and data reduction. The talk will comment on the setup of an HP experiment, sample screening and pre-experimenting. It will discuss the HP strategies. The instrument video feature can be used to gather sample shape information and the size of the gasket hole. The new EwaldPro reciprocal space viewer simplifies the way how to obtain unit cells from HP experiments. New options in data reduction (dc proffit) help to obtain even better HP data then before. At the post-processing step CrysAlisPro now interfaces with Ross Angle's program Absorb for HP cell corrections and allows seamless correction with empirical methods as well. Finally some comments on synchrotron experimentation are made.



Posters

Rietveld refinement of the $\text{Ca}_9\text{R}(\text{VO}_4)$ (R = La, Nd, Gd) compounds

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Compounds of the $\text{Ca}_9\text{R}(\text{VO}_4)$ belong to a large family of whitlockite-type materials (space group $R3c$). Some of them are known to be applicable, e.g., for white-light emitting LEDs, as discussed in Refs. [1], [2]. The results of structure refinement for $\text{Ca}_9\text{La}(\text{VO}_4)_7$, $\text{Ca}_9\text{Nd}(\text{VO}_4)_7$ and $\text{Ca}_9\text{Gd}(\text{VO}_4)_7$ samples prepared by solid-state reaction have been reported in Refs. [3], [4] and [4], respectively. In the present work, characterization of $\text{Ca}_9\text{R}(\text{VO}_4)$ single crystals by determination of their orientation and structure is presented. The structure of polycrystalline samples prepared from perfect single crystals grown by Czochralski growth method is studied. The powder diffraction experiments were performed using a laboratory Panalytical XPERT MPD diffractometer equipped with a Ge monochromator and a strip detector. The crystals were verified to adopt the [001] orientation of the applied seed. Phase analysis has shown that the crystals are pure $\text{Ca}_9\text{R}(\text{VO}_4)$ phases. The results of refinements show a consistency with scarce literature data. Similarities and differences between the present data and the literature ones will be discussed.

References

- [1] X. Wu, Y. Huang, H. J. Seo, *Ceramics Int.*, **37** (2011) 2323.
- [2] L. Liu, R.-J. Xie, N. Hirotsaki, Y. Li, *J. Spectrosc. Dyn.*, (2013) 3.
- [3] A. A. Belik, V. A. Morozov, R. N. Kotov, S. S. Khasanov, B. I. Lazoryak, *Crystallogr. Rep.*, **42** (1997) 751.
- [4] A. A. Belik, V. A. Morozov, S. V. Grechkin, S. S. Khasanov, B. I. Lazoryak, *Crystallogr. Rep.*, **45** (2000) 798.

High-pressure Crystallization of DL-Mandelic Acid Racemate

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Mandelic acid, $C_6H_5CHOHCOOH$, MA (Scheme 1), is one of frequent exempts from the Wallach's rule, as its racemate DL-MA is less dense than the enantiomers. This relation appears unfavourable for the racemate stability at high-pressure, however the racemate remains more stable than the conglomerate of enantiomers up to 1.36 GPa at least. The isochoric crystallization of DL-MA yields its orthorhombic form I, space group $Pbca$, and above 0.65 GPa another centrosymmetric polymorph of monoclinic DL-MA form II, space group $P2_1/c$, becomes stable [1]. Their structures have been determined by X-ray diffraction of the single crystals *in situ* grown in a diamond-anvil cell (DAC) up to 1.36 GPa (Figure 1). Lattice-energy calculations by the semiempirical PIXEL method demonstrate that DL-MA form II is more stable than DL-MA form I, and both these racemates are more stable than their enantiomer counterpart L-MA.

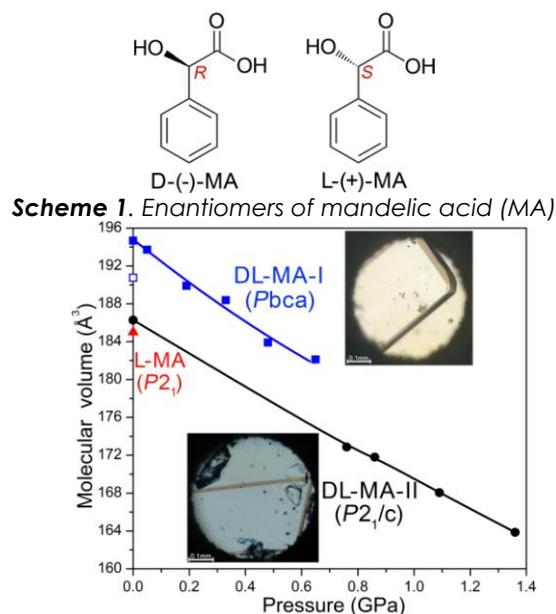


Figure 1. The molecular volume V_m (V/Z) of DL-MA in the function of pressure at 296 K for DL-MA-I (blue squares) and DL-MA-II (black circles). Also, the DL-MA at 0.1 MPa/150 K (blue open square) and L-MA (red triangle, ref 2) have been indicated. The insets show the crystal habits of DL-MA-I and II, as observed in the DAC.

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References

- [1] I. B. Rietveld, M. Barrio, J.-L. Tamarit, B. Do, R. Céolin, *J. Phys. Chem. B*, **115** (2011) 14698.
 [2] A. O. Patil, W. T. Pennington, I. C. Paul, D. Y. Curtin, C. E. Dykstra, *J. Am. Chem. Soc.*, **109**, (1987) 1529.

Crystal structure of gold(I) diethyldithiocarbamate coordination polymer

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The discovery of sandwich complexes caused a rapid progress in the research on metalloorganic and coordination chemistry. Many reports about new applications and uses of metalloorganic and coordination compounds have been published. Some of noble-metal complexes found application in medicine, for example cis-platin[1] in anticancer therapy and auranofin[2] used in treatment of rheumatoid arthritis. Some complexes, due to their luminescence properties were used as a photochemical sensors[3]. It has been noticed that gold(I) complexes stabilized by the bridging ligands tend to form dimeric, oligomeric or even polymeric structures through the interactions of gold atoms. Since 1989, such interactions are defined as aurophilic interaction.

In a reaction of PPh_3AuCl with sodium diethyldithiocarbamate in methanol we have obtained crystals of gold(I) diethyldithiocarbamate. The title compound forms orthorhombic crystals, space group $Fddd$. Moreover, the gold ions are bridged through aurophilic interaction into infinite subtly wavy chains.

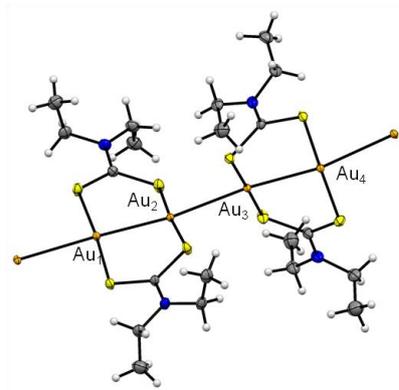


Fig. 1 Structure of $[\text{Au}_4(\text{C}_4\text{H}_{10}\text{NCS}_2)_4]_n$ complex.

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References

- [1] B. Rosenberg, L. VanCamp, J. E. Trosko, V. H. Mansour, *Nature*, **222** (5191) 385.
- [2] I. Kim, J. Jin, I. Lee, S. Park, *Br. J. Pharmacol.*, **142** (2004) 749.
- [3] L. H. Gade, *Angew. Chem. Int. Ed.*, **11** (1997) 1171.

Racemic and enantiopure *N*-benzoyl-*N'*-(1-phenylethyl)thiourea

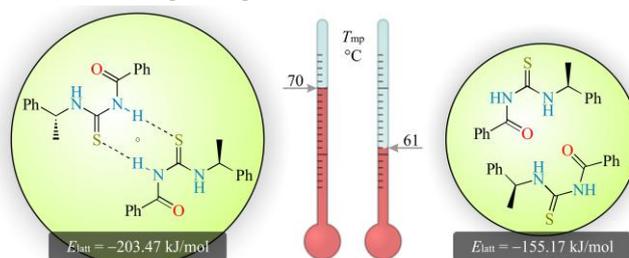
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Relation between crystal packing and presence or absence of inversion center has been a subject of interest for many years [1]. Difference in stability of racemic and enantiopure crystals is still actively investigated [2, 3]. According to Wallach's rule, a racemic crystals tends to have a denser packing than those composed of corresponding homochiral molecules [4, 5]. This rule is often broken hence its validity was studied [6].

Within this work racemic (*RS*)-*N*-benzoyl-*N'*-(1-phenylethyl)thiourea (**1**) and chiral (*S*)-*N*-benzoyl-*N'*-(1-phenylethyl)thiourea (**2**) have been synthesized following the procedure given in [7] and characterized using NMR, IR and UV-Vis spectroscopy, melting point and X-ray single-crystal diffraction analysis. First compound crystallizes in space group *C2/c* and centrosymmetric dimers are found in its structure as it is common among similar compounds. The second one crystallizes in space group *P2₁2₁2₁* and such dimers are not formed. Experimental data on related (*R*)-*N*-benzoyl-*N'*-(1-phenylethyl)thiourea is available for oil form only, so the crystal structure and melting point are unknown [8].

We found that enantiopure thiourea **2** have denser crystal packing than racemic one. On the other hand, melting point of racemic crystal **1** was higher, what may imply grater crystal lattice stabilization. Because these facts were contradictory, theoretical methods were used to determine respective lattice energies. Stability of these two forms was evaluated by means of first-principles lattice energy calculations [9, 10].



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References

- [1] J. D. Dunitz, *Acta Cryst. B* **51** (1995) 619-631.
- [2] A. R. Kennedy, C. A. Morrison, N. E. B. Briggs, W. Arbuckle, *Cryst. Growth Des.*, **11** (2011) 1821.
- [3] P. S. Navare, J. C. MacDonald, *Cryst. Growth Des.*, **11** (2011) 2422.
- [4] O. Wallach, *Liebigs Ann. Chem.*, **286** (1895) 90.
- [5] O. Wallach, *Liebigs Ann. Chem.*, **286** (1895) 119.
- [6] C. P. Brock, W. B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.*, **113** (1991) 9811.
- [7] I. B. Douglass, F. B. Dains, *J. Am. Chem. Soc.*, **56** (1934) 719.
- [8] D. Ma, K. Cheng, *Tetrahedron: Asymmetry*, **10** (1999) 713.
- [9] S. Tsuzuki, H. Orita, K. Honda, M. Mikami, *J. Phys. Chem. B*, **113** (2010) 6799.
- [10] S. Tsuzuki, H. Orita, H. Ueki, V. A. Tsuzuki, *J. Fluor. Chem.*, **131** (2010) 461.

Dithiazyl Radicals - Structures and Charge Densities of their Crystals and Co-Crystals

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Purely organic systems can exhibit conductivity, superconductivity or magnetically ordered phases - properties usually thought as restricted only for crystals containing metallic centres (Cu, Mn, etc.). One of the most intriguing groups of such systems is a family of thiazyl radicals.[1] These radicals are chemically stable, so they can be arranged in closely packed structures. Relatively high electrostatic polarization allows for inter- and intramolecular S...N interactions. In the crystal phase, the thiazyl group often co-exists with a phenyl molecular fragment, which further stabilizes the crystal lattice by introducing an intermolecular $\pi... \pi$ aromatic interactions (e.g. phenyl...perfluorophenyl stack interaction). The spin structure of these compounds is strongly coupled to the crystal structure. One can then try to adjust the magnetic properties (e.g. FM-AFM ordering) of such systems by small changes of structural parameters (e.g. distances between molecules in stack). This and other intriguing properties suggest that the dithiazyl radicals are promising candidates for the construction of molecular devices. No experimental electron density distribution of such system in the crystal phase has been accomplished so far. The scope of the work was to determine the quantitative electron density distribution and its parameters (ρ and $\Delta\rho$ in critical points, integrated charges, etc.) for the three very interesting model crystals of thiazyl radicals belonging to dithiadiazolyl family.[2] The Hansen-Coppens multipole expansion of electron density model was refined against the high resolution ($\sin\Theta / \lambda > 0.7\text{\AA}^{-1}$) X-ray diffraction data to obtain the best models of the electron density distribution in given crystals. These models were then used to calculate quantitative electron density properties using the Bader's QTAIM theory such as critical points parameters (ρ_{CP} , $\Delta\rho_{\text{CP}}$, bond paths), atomic basins or integrated electron density parameters (integrated charges, atomic multipoles and volumes, etc). The obtained results and detailed analysis of dithiadiazolyl radicals should hopefully help in a better understanding of the magnetic phenomena in organic systems.

References

- [1] J. M. Rawson, A. Alberola, A. Whalley, *J. Mater. Chem.*, **16** (2006), 2560.
- [2] C. Allen, D.A. Haynes, C.M. Pask, J.M. Rawson, *CrystEngComm*, **11** (2009), 2048.

Menthol – mint racemate

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Menthol is an organic compound naturally occurring in mint plants. It is also synthetically manufactured. There is evidence [1] that menthol has been known in Japan for more than 2000 years, but in the West it was not isolated until 1771, by Hieronymus David Gaubius [2]. Natural menthol exists predominantly as one pure stereoisomer, nearly always the (1*R*,2*S*,5*R*) form.

The physico-chemical properties of the levo- and dextrorotatory menthol isomers as well as the corresponding racemic compound were studied using X-ray single-crystal or powder diffraction and differential scanning calorimetry experiments [3]. Moreover, the stable and metastable experimental temperature-composition phase diagrams of the L-menthol/D-menthol binary system were determined [4]. This provides new physical, chemical and thermodynamic data of L-, D- and DL-menthol and offers new insight into their polymorphism as well as into the levorotatory–dextrorotatory menthol interactions.

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References

- [1] J. L. Simonsen, *The Terpenes*, Cambridge University Press, **1** (1947) 230.
- [2] *Adversoriorum varii argumentii, Liber unus*, Leiden, (1771) 99.
- [3] M. Kuhnert-Brandstaetter, R. Ulmer, L. Lanaghammer, *Arch Pharm.*, **307** (1974) 497.
- [4] (a) Y. Corvis, P. Negrier, M. Lazerges, S. Massip, J.-M. Leger, P. Espeau, *J. Phys. Chem. B*, **114** (2010) 5420. (b) Y. Corvis, P. Negrier, S. Massip, J.-M. Leger, P. Espeau, *CrystEngComm*, **14** (2012) 7055.

Argentophilicity in silver(I) dithiocarbamates

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Metal-metal interactions belongs to the less strong and most unusual type of intermolecular short contacts, especially in gold(I) [1] and silver(I) [2] complexes. The "argentophilicity" describes the short silver-silver interactions, where the distance between two metal centers is lower than the sum of van der Waals radii. Moreover, these structural motif can be employed in crystal engineering and variety of chemical architectures, such as clusters or polymers, can be obtained.

In our work we have focused our attention on synthesis and crystal structure of simple silver(I) complexes with S-donor dithiocarbamate ligands. Silver(I) diethyl-dithiocarbamate was obtained in the reaction of sodium diethyldithiocarbamate with silver(I) nitrate. A single, monoclinic crystal of silver(I) complex was grown in methanol solution. Interestingly, the dithiocarbamate ligands can be classified as intra-molecule tetradentate and coordinate to the metal centers. In the molecular arrangement a motif of argentophilic interactions can be observed between two silver(I) cations. The structural details will be presented.

References

- [1] F. Baril-Robert, M. A. Radtke, C. Reber, *J. Phys. Chem.*, **116** (2011) 2192.
- [2] H. Yamaguchi, A. Kido, T. Uechi, K. Yasukouchi, *Bull. Chem. Soc. Jpn.*, **49** (1976) 1271.

Hydrogen bonds NH \cdots N in compressed benzimidazole polymorphs

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Compounds with switchable NH \cdots N bonds are promising new ferroelectric and relaxor materials with desired dielectric properties.[1,2] Therefore the structure-property relation of NH \cdots N bonds in different molecular environments are of primary importance for selecting chemical substances and engineering new materials of this kind. Hence we have focused our interest at benzimidazole (BzIm). Its molecule consists of fused benzene and imidazole rings and like imidazole,[3] BzIm molecules form NH \cdots N hydrogen bonded polar chains of molecules in its structure.

Two phase transitions in compressed BzIm polymorphs reveal a remarkable interplay of the H-site in NH \cdots N hydrogen-bonded aggregates and the crystal structure when exposed to high-pressure.[4] The ambient-pressure polar polymorph α , space group $Pna2_1$ (unit-cell parameters at ambient pressure: $a = 13.098 \text{ \AA}$, $b = 6.764 \text{ \AA}$, $c = 6.963 \text{ \AA}$, $V/Z = 159.27 \text{ \AA}^3$), at $p_1 = 0.26 \text{ GPa}$ transforms into centrosymmetric phase β , space group $Pccn$ (unit-cell parameters at 0.62 GPa: $a = 9.605 \text{ \AA}$, $b = 16.021 \text{ \AA}$, $c = 7.4386 \text{ \AA}$, $V/Z = 143.06 \text{ \AA}^3$) and above $p_2 = 2.26 \text{ GPa}$ into another centrosymmetric polymorph γ , space group $Pbca$ (unit-cell parameters at 2.90 GPa: $a = 9.782 \text{ \AA}$, $b = 7.859 \text{ \AA}$, $c = 12.967 \text{ \AA}$, $V/Z = 124.60 \text{ \AA}^3$). Single crystals of forms α , β and γ have been *in-situ* grown in isothermal and isochoric conditions in a diamond-anvil cell and their structures determined by X-ray diffraction.

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References

- [1] M. Szafrński, A. Katrusiak, G. J. McIntyre, *Phys. Rev. Lett.*, **89** (2002) 5507.
- [2] A. Katrusiak, M. Szafrński, *J. Am. Chem. Soc.*, **128** (2006) 15775.
- [3] D. Paliwoda, K. F. Dziubek, A. Katrusiak, *Cryst. Growth Des.*, **12** (2012) 4302.
- [4] W. Zieliński, A. Katrusiak, *Cryst. Growth Des.*, **13** (2013) 696.

Unusual properties of novel ferroelectrics: croconic acid

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Croconic acid, $C_5H_2O_5$, 4,5-dihydroxycyclopent-4-ene-1,2,3-trione, was recently reported to exhibit ferroelectric properties till it decomposes at 450 K [1]. Owing to its dielectric characteristics, and most importantly its ferroelectric properties retained at normal conditions, croconic acid is a promising material for potential optoelectronic applications. Most of ferroelectric materials undergo phase transitions at Curie temperature (T_c), above which their spontaneous polarization disappears and the substance becomes paraelectric. No such a transition has been found in croconic acid.

It is characteristic of prototypic ferroelectric KH_2PO_4 (KDP) and most other $OH\cdots O$ bonded ferroelectric crystals that their T_c associated with paraelectric phase decreases at high pressure. The negative $\partial T_c/\partial p$ in KDP and in antiferroelectric squaric acid, which is a close analogue of croconic acid, is generally connected to the compressed $O\cdots O$ distance. Our high-pressure X-ray diffraction structural and Raman spectroscopy studies on croconic acid have not detected the paraelectric phase up to 5.3 GPa.

Croconic acid crystallizes in orthorhombic polar space group $Pca2_1$, but its structure approximates centrosymmetric space group $Pcam$ [2,3]. This higher symmetry is broken by H-atoms ordered off-center sites in the $OH\cdots O$ bonds and by small displacements of other atoms. The results of our study suggest that there is a distinct group of $OH\cdots O$ bonded ferroelectrics which have no paraelectric phase at all. This is a highly desirable feature for possible applications, which extends the temperature range of the ferroelectric properties and eliminates the reduction of spontaneous polarization close to T_c .

In our work we have investigated the structural transformations in croconic acid in high pressure and explained the structural origins of its unexpected behaviour.

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References:

- [1] S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai, Y. Tokura, *Nature*, 463 (2010) 789.
- [2] S. Horiuchi, Y. Tokura, *Nature Materials*, 7 (2008) 357.
- [3] G. J. Piermarini, S. Block, J. D. Bernett, R. A. Forman, *J. Appl. Phys.*, 46 (1975) 2774.

High-pressure powder diffraction in laboratory

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Preliminary studies of high-pressure effect on substances can be done by powder X-ray diffraction in laboratory. A modified Merrill-Bassett diamond-anvil cell (DAC) [1] and a standard four-cycle diffractometer with MoK α or AgK α radiation in many cases suffices for testing the sample stability and for determining the pressure of its transformation.

The procedure for preparation and centering of DAC and performing of the high-pressure powder measurement is similar to the single crystal method. Powder sample is precisely grained and placed in the opening of the metal gasket along with small piece of ruby and addition of hydrostatic medium. After each increase of the pressure diffraction experiment is performed. Collected images are processed in order to cover intense reflections of diamonds from DAC and powder diffractogram is generated with program CrysAlisPro [2]. Data can be exported and after subtraction of the background produced by DAC, they are ready to be compared and analyzed.

The crucial factor for high-pressure powder experiment is that the opening in the gasket, diameter of the primary beam and positioning of the DAC during the measurement must be precisely selected and correlated in order to avoid incidence of X-ray beam on the gasket and simultaneously to allow the widest possible coverage of the sample. That is why opening in the gasket cannot be either smaller or much bigger than the diameter of the incident beam, special collimator is used in order to obtain beam with the diameter of 0.3mm and the run list is specially adapted.

High-pressure powder experiment is a perfect way for fast verification of the pressure influence on the sample. It is very convenient method for designating the phase transition pressure without the necessity of performing many, time-consuming and sensitive single-crystal experiments.

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References

- [1] Merrill, L., Bassett, W. A. *J. Rev. Sci. Instrum.*, **45** (1974) 290.
- [2] Oxford Diffraction, CrysAlis CCD, Data collection GUI for CCD and CrysAlis RED, CCD data reduction GUI versions and 1.17.13 beta, Oxford Diffraction, Poland 2003.

Structure and elastic properties of praseodymium orthovanadate

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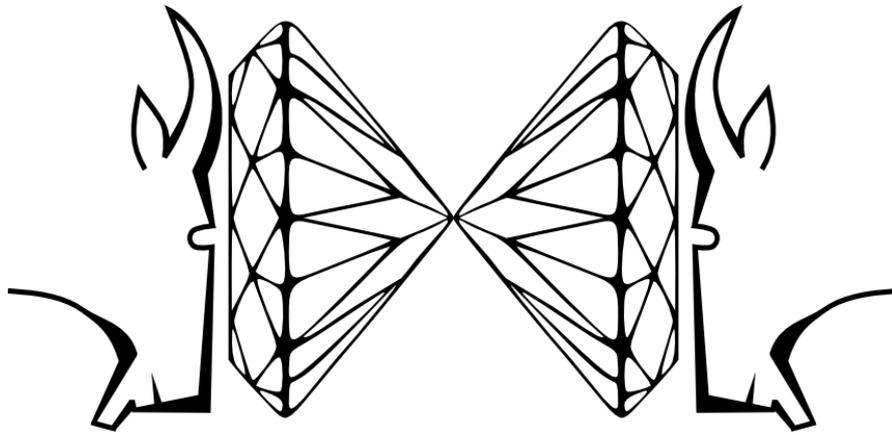
Physical and optical properties of rare-earth orthovanadates (RVO₄) allow them to be applicable in optical devices, gas sensors, phosphors, polarizers, etc.; they are also useful in catalysis [1–6]. At ambient conditions most of RVO₄ materials adopt the zircon structure (space group *I*₄₁/*amd*). In the 5 – 10 GPa pressure range these materials undergo a phase transition from zircon to scheelite-type structure (space group *I*₄₁/*a*).

The aim of present investigation was to determine structure parameters and elastic properties for zircon and scheelite phases of praseodymium orthovanadate (PrVO₄). Both samples were prepared in polycrystalline form using solid state reaction. The investigation of structure properties for both phases was performed using laboratory Philips X'Pert Pro MPD Alpha1 diffractometer equipped with an incident beam germanium monochromator and a strip detector. Structure parameters for the samples held in ambient conditions were refined by the Rietveld method using the FullProf software. Energy dispersive data at high-pressure conditions were collected using white synchrotron radiation at the F2.1 beamline (HASYLAB/DESY, Hamburg, Germany). The in-situ powder-diffraction experiments were carried out using the MAX80 X-ray diffraction press in pressure range up to 6 GPa. The data were collected using a germanium solid-state detector. Unit cell parameters were refined using the Le Bail method. Bulk moduli for zircon and scheelite phases of praseodymium orthovanadate were calculated from fitting of the second order Birch-Murnaghan equation of state.

In the present investigation, structure parameters and the equation of state parameters for zircon and scheelite structures of praseodymium orthovanadate were obtained experimentally. The results are discussed and compared with scarce literature data existing for studied material.

References

- [1] R.A. Fields, M. Birnbaum, C.L. Fincher, *Appl. Phys. Lett.*, **51** (1987) 1885.
- [2] A.I. Zagumennyi, V.G. Ostroumov, I.A. Shcherbakov, T. Jensen, J.P. Meyen, G. Huber, *Sov. J. Quantum Electron.*, **22** (1992) 1071.
- [3] A.A. Kaminskii, K. Ueda, H.J. Eichler, Y. Kuwano, H. Kouta, S.N. Bagaev, T.H. Chyba, J.C. Barnes, G.M.A. Gad, T. Murai, J. Lu, *Optics Commun.*, **194** (2001) 201.
- [4] E.V. Tsipis, M.V. Patrakeev, V.V. Kharton, N.P. Vyshatko, J. R. Frade, *J. Mater. Chem.*, **12** (2002) 3738.
- [5] M. Yu, J. Lin, S.B. Wang, *Appl. Phys. A: Mater. Sci. Proc.*, **80** (2005) 353.
- [6] F. Chen, X. Wang, S. Li, G. Fu, K. Wang, Q. Lu, D. Shen, R. Nie, H. Ma, *J. Appl. Phys.*, **94** (2003) 4708



Laboratory work

High-Pressure Laboratories

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High-pressure technique is becoming more popular tool for crystallization. However, the beginnings were not easy. First devices used for high-pressure experiments were big and the access to the studied substance was limited. [1] The next step was applying diamonds for generating high pressure. [2, 3] A breakthrough was inventing miniature diamond anvil cell in 1974 [4] and applying a ruby fluorescence method for pressure calibration. [5] Since then Diamond anvil cell (DAC) has become a convenient device for high-pressure experiments. Application of DAC enables people to learn and to understand the behavior of different substances in extreme conditions, the synthesis of compounds that are difficult to obtain at normal conditions and the nature of intermolecular interactions. High-pressure experiments are more convenient than the low-temperature measurements and give the opportunity to choose the crystallization method (isothermal, isochoric). [6]

High-pressure laboratories are dedicated to practical exercises with the diamond-anvil cell (DAC), its assembling and loading with samples, centering the DAC on a CCD diffractometer, diffraction data collection and processing. Isothermal and isochoric crystallizations will be applied for growing single crystals of new phases of substances brought in by participants. The laboratories will include theoretical and practical parts for both beginner and expert high-pressure crystallographers. The aim of this workshop is to encourage the participants to start high-pressure experiments in their laboratories.



Fig. 1 Diamond anvil cell.

References

- [1] P. W. Bridgman, *Review of Modern Physics*, **18** (1946) 1.
- [2] A. W. Lawson, T. Y. Tang, *Rev. Sci. Instrum.*, **21** (1950) 815.
- [3] J. C. Jamieson, A. W. Lawson, N. D. Nachtrieb, *Rev. Sci. Instrum.*, **30** (1957) 1016.
- [4] R. A. Forman, G. J. Piermarini, J. D. Barnett, S. Block, *Science*, **176** (1972) 284.
- [5] L. Merrill, W. A. Bassett, *Rev. Sci. Instrum.*, **45** (1974) 290.
- [6] A. Katrusiak, *Acta Cryst.*, **A64** (2008) 135.