

material. For this, backing plates made of polycrystalline beryllium, which satisfies both criteria, have often been chosen. However, this metal presents several disadvantages. Besides its high toxicity and temperature sensitivity which limits its use to studies at moderate temperatures, it produces spotted and broad diffraction rings which influence large part of the background and can significantly impair measurement of weaker diffraction spots of investigated crystals. Miletich et al. [1] proposed diamond plates as an alternative anvil support. In the present study a comparison between high pressure structural data acquired using two DACs with the same construction (ETH-type) but equipped with diamond or beryllium backing plates, respectively, is presented in order to evaluate directly the possible improvements in data. A synthetic single crystal of $\text{NaInSi}_2\text{O}_6$ pyroxene was selected for the study and loaded consecutively into the two cells in equal orientation. Intensity data were collected using a Bruker-AXS four circle diffractometer equipped with a Smart1000 CCD area detector and a crystal of quartz was used as an internal pressure standard. The SMART [2] software was used for the data collection, SAINT+ [2] for the integration and reduction of data and ABSORB V.6.0 [3] for the absorption correction. The measurement strategy and the calculation procedures were equal in order to perform a reliable comparison. As already indicated by [1] the use of a low absorbing single crystal as a replacement of the commonly used polycrystalline beryllium as backing-plate material reduces the unwanted background from broad powder rings to only a few strong spots of a kind already present and originating from diamond anvils. We can prove a significant improvement in data quality as witnessed by better reliability factors in structure refinement and lower errors on the atomic coordinates, thermal parameters and average bond lengths. The resulting structural data are more reliable and able to reveal more subtle structural changes under pressure. The differences between the two structure refinements will be illustrated and discussed in detail.

[1] Miletich R., Allan D.R., Kuhs W.F., *Rev. Mineral. Geochem.* 2000, 41, 445. [2] Bruker-AXS products. [3] Angel R.J., *J. Appl. Crystallogr.* 2004, 37, 486.

Keywords: Diamond Anvil Cell, Single crystal X-ray diffraction, Be and diamond backing-plates

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Two novel ($\text{V}_{18}\text{O}_{42}$)-Isopolyoxovanadates. Sebastian Prinz, Georg Roth. *Institut für Kristallographie, RWTH Aachen, Germany.*

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Vanadium(IV) is found in a wide variety of different structures ranging from spin chains to square lattices to the cage-like polyoxovanadates. These materials often display interesting magnetic properties due to geometrical frustration of the spin-(1/2) centres. Dark brown single crystals were obtained from a mixture of caesium/rubidium hydroxide and vanadyl sulphate by hydrothermal synthesis at 240°C and autogenous pressure in Teflon-lined Parr autoclaves for three days. The furnace was then turned off and the autoclaves were left to cool down to room temperature. Novel Cs- and Rb-compounds with ($\text{V}_{18}\text{O}_{42}$)-cluster anions hosting single water molecules were obtained. The structure of these compounds was studied by single crystal X-ray diffraction on an Imaging Plate Diffraction System (IPDS II). It was found that both

compounds consist of anionic clusters of 18 VO_5 pyramids sharing edges and corners similar to those found by Müller and co-workers [1]. Cs and Rb ions compensate for the negative charge carried by the complex anions. Both compounds have similar crystal structures but contain less H_2O and crystallize in different space group symmetry than those characterized by Müller and co-workers. In our contribution we give a detailed description of the crystal structure and discuss the differences with the latter.

[1] Müller, A. et al., *Inorg. Chem.*, 1997, 36, 5239.

Keywords: polyoxovanadate, spin 1/2, hydrothermal

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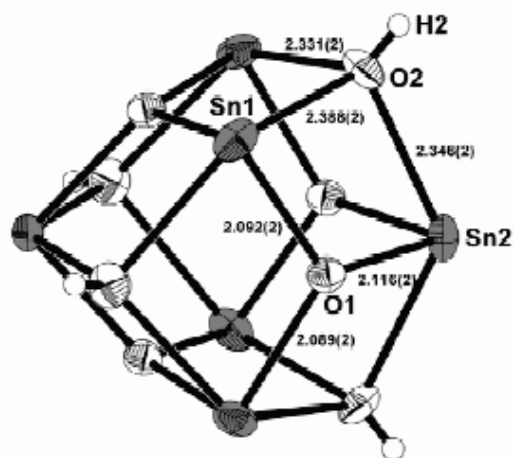
Low temperature, single crystal X-ray data of synthetic hydromarchite, $\text{Sn}_6\text{O}_4(\text{OH})_4$. Hans

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Aqueous solutions of tin(II) salts contain a lot of different mono- and polynuclear, cationic or anionic, oxo-hydroxo species depending on its salt and proton concentrations. From neutral solutions, colorless tin(II) monoxide, SnO , separates in form of a bad defined, voluminous, water insoluble precipitate, containing different amounts of water. A stoichiometric exact hydrate of composition, $\text{SnO} \cdot 1/3\text{H}_2\text{O}$, can only be prepared on certain conditions. Some older structure investigations [1],[2] reveal that this compound is a polynuclear molecular oxide hydroxide with formula $\text{Sn}_6\text{O}_4(\text{OH})_4$. This compound is also known to be a so-called anthropogenic mineral because archeologists found it on many tin objects which were covered for long periods by water. In mineralogy this compound is named hydromarchite.

Because it is difficult to grow appreciate single crystals on this compound our knowledge about its structure are limited. By chance we found single crystals of the title compound which were of high quality and large enough for X-ray diffraction experiments, in a more than ten years old sample of $^n\text{BuSnH}_3$ in toluene.



$\text{Sn}_6\text{O}_8\text{H}_4$: tetragonal, $P-42_1c$ (no. 114), $a = 7.8809(2) \text{ \AA}$, $c = 9.0595(4) \text{ \AA}$, $V = 562.67(3) \text{ \AA}^3$, $Z = 2$, $d_{\text{cal}} = 4.983 \text{ g/cm}^3$,

$\mu(\text{MoK}\alpha) = 13.124 \text{ mm}^{-1}$, $F_{000} = 736$, $2\theta_{\text{max}} = 70^\circ$, 24673 reflection collected, 1243 unique reflections, $R_{\text{int}} = 0.0298$, multi-scan absorption correction, $T_{\text{min}} = 0.3161$, $T_{\text{max}} = 0.3718$, completeness 100%, 35 parameters refined, absolute structure parameter = 0.04(5), $R_1 [I > 2\sigma(I)] = 0.0149$, $R_1 [\text{all data}] = 0.0289$, $wR_2 [I > 2\sigma(I)] = 0.0157$, $wR_2 [\text{all data}] = 0.0291$, $\Delta e_{\text{max}} = 0.775 \text{ e}\text{\AA}^{-3}$, $\Delta e_{\text{min}} = -0.748 \text{ e}\text{\AA}^{-3}$.

[1] Howie, R. A.; Moser, W. *Nature* 1968, 219, 372-373. [2] Abrahams, I.; Grimes, S. M.; Johnston, S. R.; Knowles, J. C. *Acta Crystallogr.* 1996, C52, 286-288.

Keywords: tin oxide compounds, mineral, precise crystal structure analysis

FA2-MS16-P48

Structure and magnetic properties of new triple molybdates $\text{CsMZr}_{0.5}(\text{MoO}_4)_3$ ($M = \text{Al, Ga, In, Sc, Cr, V, Fe}$). Angelina Sarapulova^a, Tuyana Namsaraeva^b, Daria Mikhailova^{a,c}, Björn Schwarz^a, Helmut Ehrenberg^a, Zhibzema Bazarova^b, Bair Bazarov^b. ^a*Institute for Complex Materials, IFW Dresden, Germany.* ^b*Baikal Institute of Nature Management, Siberian Division, Russian Academy of Science, Russia.* ^c*Institute for Materials Science, Darmstadt University for Technology, Germany.*
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Isostructural complex molybdates $\text{CsMZr}_{0.5}(\text{MoO}_4)_3$ ($M = \text{Al, Ga, In, 3d-elements}$) demonstrate a variety of physical-chemical, electrophysical and optical properties depending on the trivalent cation. The crystal structures of $\text{CsAlZr}_{0.5}(\text{MoO}_4)_3$ and $\text{CsFeZr}_{0.5}(\text{MoO}_4)_3$ phases were refined from single-crystal X-ray diffraction [1, 2]. The structure represents a three-dimensional framework of corner-shared MoO_4 -tetrahedra and $(\text{M,Zr})\text{O}_6$ -octahedra (S.G. R-3); the channels along the *c*-axis are filled by Cs-ions, which should provide high ionic conductivity at elevated temperatures.

In our work, the compounds with $M = \text{Al, Ga, In, Sc, Cr, V, Fe}$ were synthesized by solid state reaction in air or in a sealed silica tube (for $M = \text{V}$) and investigated by X-ray powder diffraction with a STOE STADI P diffractometer (Mo-K α_1 -radiation). All diffraction patterns were analyzed by full-profile Rietveld refinements, using the software package WinPLOTR [3]. Magnetic properties have been studied with a superconducting quantum interference device (SQUID) from Quantum Design.

The lattice parameters of $\text{CsMZr}_{0.5}(\text{MoO}_4)_3$ increase nonlinearly with increasing radius of the trivalent element M. The same correlation is observed for the melting point of these phases. Investigation of magnetic properties of the compounds with 3d transition metals Cr, Fe and V showed a paramagnetic behaviour below room temperature and a deviation between field-cooled and zero-field cooled data below ca. 10 K, indicating a ferro- or ferrimagnetic ordering. However, since this is rather unusual for such magnetic diluted frameworks, because the interatomic distances M-M for $M=\text{V, Cr}$ and Fe in $\text{CsMZr}_{0.5}(\text{MoO}_4)_3$ are about 5.5 Å, and the 9e-site in the structure is occupied statistically with a magnetic cation only by 2/3 and with Zr by 1/3, the presence of a spin-glass type behavior is discussed.

[1] Namsaraeva T., Bazarov B., Klevtsova R., Glinskaya L., Fedorov K., Bazarova Zh. *Russian Journal of Inorganic Chemistry*, 55 (2010) 209-214. [2] Bazarov B.G., Namsaraeva T.V., Klevtsova R.F., Bamburov V.G., Glinskaya L.A., Tushinova Yu.L., Bazarova Zh.G. and Fedorov K.N. *Doklady Physical Chemistry*, 431 (2010) 43-47. [3] Roisnel T., Rodriguez-Carvajal J., *Mater. Sci. Forum*, 378-381 (2001) 118-123.

Keywords: three-dimensional framework, channel structure, ionic conductivity

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High-temperature elastic properties of sanidine. Pia Schröder, Peter Sondergeld, Jürgen Schreuer. *Institute of Geology, Mineralogy and Geophysics, Ruhr University Bochum, Germany.*

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Sanidine crystals from the Eifel, Germany, are well-known for irreversible changes of their optical properties at moderately high annealing temperatures (starting from about 750°C), which are probably related to changes in the Al/Si order [1]. Polarised infrared spectra and NMR studies indicate a relatively high amount of water in the Eifel sanidines (~ 200 wt-ppm), compared to low-sanidine crystals from Madagascar (~ 1 wt-ppm) [2,3]. The sanidine megacrystals from the Eifel are further characterised by very low concentrations of dislocations indicating hydrothermal growth conditions [4]. However, the reason for the rapid changes of their optical properties is still not understood.

We studied the elastic behaviour of sanidines from various eruptive centres of the Eifel and from Madagascar (served as a reference) between room temperature and 1100°C using resonant ultrasound spectroscopy. All samples were of gem-quality without visible inclusions or cracks.

The elastic properties of our 'dry' Madagascar sanidine agree well with literature values obtained by the plate-resonance technique close to room temperature [5]. The temperature evolution of the elastic constants is fully reversible without any discontinuity. Remarkable is the positive temperature coefficient of the shear stiffness c_{44} which is related to the structural instability driving the ferroelastic phase transition in Na-rich alkali-feldspars due to framework shearing. Additionally, a small ultrasound dissipation peak appears at about 890°C.

On the other hand, 'hydrous' sanidines from the Eifel show reversible exponential increase of ultrasound dissipation above 800°C, followed by rapid irreversible softening of all resonance frequencies by about 8 % above 970°C. The latter phenomenon is most likely related to the development and propagation of micro-cracks in the sample. Both effects are probably caused by the increasing mobility and eventually the loss of water dissolved in the crystal structure of these nominally anhydrous minerals. The high mobility of the water molecules allows for a new, less ordered Al/Si equilibrium state to be reached on the time scale of the experiment. The associated increase of the configurational entropy leads to elastic softening of the macroscopic crystals.

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Keywords: sanidine, elasticity, cation ordering