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ON THE ELASTIC BEHAVIOUR OF ZEOLITE PAULINGITE: A SYNCHROTRON POWDER DIFFRACTION STUDY

R. Skála[1,2], G. D. Gatta[3], Y. Lee[4]

[1]Inst. of Geology AV ČR, Rozvojová 269, 16500 Praha 6, Czech Republic
[2]ÚGMNZ, Faculty of Science, Charles University, Albertov 6, 12843 Praha 2, Czech Republic
[3]Dipartimento di Scienze della Terra, Universitŕ degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy
[4] Physics Dept., Brookhaven National Laboratory, Upton, NY 11973–5000, USA
skala@gli.cas.cz

The high-pressure (HP) elastic behaviour of a zeolite paulingite found in vugs in olivine nephelinite of the Vinařická hora Hill Tertiary volcano near Kladno (Czech Republic) was studied by means of in situ synchrotron X-ray powder diffraction. The diffraction experiments were performed using a diamond anvil cell (DAC) at the X7A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. A gas-proportional position-sensitive detector was stepped in 0.25 °2 intervals over the angular range of 3–35 °2 with counting times of 90 - 150 s per step. The wavelength of the incident beam (0.60046 Å), PSD zero channel, and PSD degrees per channel were determined from a CeO_2 standard (SRM 674). A powdered sample of pauligite was placed in the gasket hole of the DAC together with some ruby chips. The pressure at the sample was measured by detecting the shift in the R1 emission line of the ruby chips with precision ± 0.1 GPa. Two sets of experiments were carried out with two different pressure-transmitting media: a nominally penetrating methanol : ethanol : water (16:3:1) mixture and a nominally non-penetrating silicon oil. The maximum pressures attained in the experiments were 5.12 GPa in the case of alcohol : water mixture and 2.53 GPa in the case of silicon oil. The chemical composition of the studied sample, $K_{4.87}Na_{0.37}Ca_{3.20}Ba_{0.23}Mg_{0.04}Sr_{0.03}Fe_{0.05}Al_{11.17}Si_{30.52}O_{84} \cdot 30 H_2O$, has been determined by an electron microprobe analyser CAMECA SX-100. Unit cell parameters were determined by LeBail whole powder pattern fitting implemented in the FullProf suite. Axial and volume bulk moduli have been calculated using a truncated second-order Birch–Murnaghan equation-of-state using program EOSFIT. No phase transition or sample decomposition have been observed up to the maximum recorded pressures. The bulk moduli refined from the data collected in nominally penetrating medium were excessively high pointing out that paulingite is over-hydrated under the conditions of the experiment. The refined elastic parameters for the experiment with nominally non-penetrating medium are: $V_0 = 43794(185)$ Å^3, $K_{T0} = 18(1)$ GPa.

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SYNTHESIS AND CRYSTAL STRUCTURES OF $Pd_3Pb_2Te_2$ AND Pd_3AgSe

F. Laufek[1], A. Vymazalová[1], M. Drábek[1], J. Drahokoupil[2], Chareev D.A.[3], Kristavchuk A.V. [3]

[1]Czech Geological Survey, Geologická 6, 152 00 Praha 5
[2]Institute of Physics of the AS CR, v.v.i., Na Slovance 2, 182 21 Praha 8
[3]Institute of Experimental Mineralogy RAS, Chernogolovka, Russia
frantisek.laufek@geology.cz

This presentation is a part of systematic research on crystal structures, phase relations and selected physical properties of phases from Pd-Pb-Te and Pd-Ag-Se ternary systems. These systems comprise many platinum-group minerals or phases, which can be found in various ore deposits as potential new minerals. Consequently, phases from these systems are of interest in mineralogy and geology of ore deposits.

The ternary compounds $Pd_3Pb_2Te_2$ and Pd_3AgSe were synthesised from elements by conventional solid-state reactions. Stoichiometric amounts of individual elements were sealed in evacuated silica glass tubes and resultant mixtures were heated at selected temperatures. Samples with $Pd_3Pb_2Te_2$ and Pd_3AgSe were heated at 400°C and 350°C, respectively. After long-term annealing, the samples were quenched in a cold-water bath. All attempts to prepare single crystals of studied phases suitable for single-crystal analysis failed, the crystal structure determinations of $Pd_3Pb_2Te_2$ and Pd_3AgSe were performed from conventional powder X-ray diffraction data. The structure solutions of title compounds by direct methods were accomplished using the program EXPO2004 [1]; subsequent refinements were performed with FullProf program.

$Pd_3Pb_2Te_2$: Space group *Pmmn*, $a = 8.59$, $b = 5.93$, $c = 6.31$ Å, $V = 322$ Å^3 and Z = 2. Its crystal structure can be described as a layered structure formed by face-shared $[PdPb_4Te_2]$ octahedra running parallel to **b** axis. Two independent palladium atoms are surrounded by four lead and two tellurium atoms showing distorted octahedral coordination with tellurium atoms in *trans* positions with respect to one another. Two independent lead atoms are coordinated by six palladium atom in two different ways. The crystal structure of $Pd_3Pb_2Te_2$ shows many structural similarities to the structure of shandite ($Ni_3Pb_2S_2$, *Rm*) and parkerite ($Ni_3Bi_2S_2$, *C*2/*m*). The phase $Pd_3Pb_2Te_2$ was described as a new mineral pašavaite [3].

Pd_3AgSe: Space group *Pa*, a = 8.63 Å, *V* = 642 Å^3 and Z = 8. The silver atom is surrounded by 12 palladium atoms, 3 selenium atoms and 1 silver atom. 12 of these atoms (9 Pd and 3 Se) form a truncated tetrahedron (Fig. 1). The other atoms (3Pd + 1 Ag) are located slightly above the centers of hexagonal faces of truncated tetrahedron. Two neighboring truncated tetrahedra share the hexagonal faces and thus form a basic structural unit of the Pd_3AgSe structure. Similarly, as was mentioned for the isostructural Au_3CaGa compound [4], the Pd_3AgSe structure show comparable local structural motives as quasicrystals. Nevertheless, Pd_3AgSe is a conventional crystalline compound. Therefore, it can be viewed as an approximant of quasikrystal [5].

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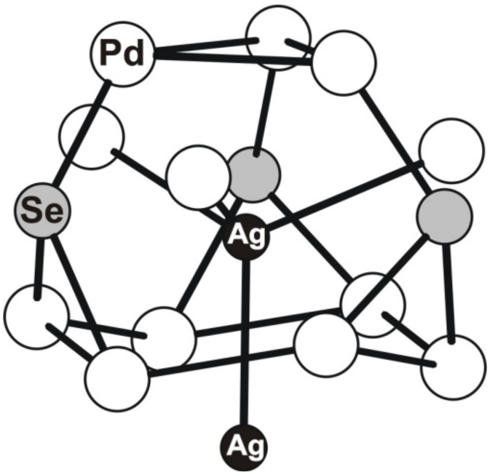

Figure 1. Coordination of Ag atoms in crystal structure of Pd_3AgSe. Note the truncated.

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ZEOLITE MEMBRANE - MFI

J. Drahokoupil[1,2] , P. Hrabánek[3,] A. Zikánová[3], M. Kočiřík[3]

[1]Institute of Physics of the ASCR, v.v.i.; Na Slovance 2, 18221 Prague 8, Czech Republic
[2]FJFI CTU in Prague, Trojanova 13,120 00 Prague 2, Czech Republic
[3]J.Heyrovský Institute of Physical Chemistry of the ASCR, v.v.i., Dolejškova 2155/3, 18223 Prague 8, Czech Republic
jandrahokoupil@seznam.cz

Introduction

The oriented zeolite MFI (ZSM-5 and silicalite-1) layers were already synthesized on different supports and showed their attractiveness for the applications in the fields of membranes [1], microreactors, sensors and optoelectronic devices. For MFI zeolite membranes, the most favorable configuration would be a thin, fully intergrown *b*-oriented layer that would exhibit higher fluxes in comparison with *a*, *c* or random oriented layers. It is also known that the orientation of crystals essentially determines the crack formation during template removal, where different expansion/shrinkage properties of MFI crystallographic axes are responsible. It has been suggested that the preparation of *a*, *b*-oriented layer is more advantageous due to the template removal [2].

Experimental

The direct hydrothermal *in*-situ syntheses of silicalite-1 layers were carried out on the surface of mercury, silicon wafer, non-porous and porous stainless steel TRUMEM^{TM} supports. The crystallizations of MFI layers were performed in the temperature range of 155-165 C under static conditions with duration of crystallization between 1 to 20 hours.

The synthesized crystal layers were washed in an ultrasonic bath, dried and further characterized with scanning electron microscope (JEOL JSM 5500LV).

The X-ray diffraction pattern were measured on PANalytical X`Pert diffractometer in Brag-Brentano geometry. The Co radiation was used.

Structure of MFI

The FMI zeolites crystallite in Pnma space group. The lattice parameters of ZSM-5 are following: *a* = 20.048, *b* = 19.884, *c* = 13.352, = 90°, lattice parameters of Silicalite-1 are a little varied. The structure contains relatively big pores which run through the structure in (100) and (010) directions. The three basic orientations ((100), (010), (001)) are shown in Fig. 1.

Diffraction pattern

Besides the low angle region, the diffraction peaks are mostly overlapped because of relatively big orthorhombic unit cell. Some important higher angle diffractions can be