



T9 - Phase Transitions, Non-Ambient Conditions

T9 - P161

IN SITU HIGH TEMPERATURE XRD STUDIES OF THE CRYSTALLIZATION OF MELT-SPUN $Mg_{63}Y_7Ni_{30}$

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Magnesium-based compounds are well-known materials for hydrogen storage. Particularly, Mg-Ni-compounds show a high hydrogen capacity. Additives of rare earth elements (Y,La,Ce) can also enhance the hydrogen absorption in such compounds [1]. Various non-equilibrium methods like intensive ball milling or rapid quenching are used to refine the microstructure and to improve the kinetics [2,3]. The $Mg_{63}Y_7Ni_{30}$ composition was selected because of the capability of hydrogen charging by electrochemical methods at room temperature for Mg-RE-TM-glasses (RE = rare earth element, TM = transition metal) and the easy-glass-formation [4]. The *in situ* high temperature X-ray diffraction allows the direct observation of the phase formation at elevated temperatures and different partial pressures.

The thermal behaviour of $Mg_{63}Y_7Ni_{30}$ was studied under hydrogen atmosphere up to 0.5 MPa in comparison with the crystallization behaviour under high-vacuum conditions.

On the other hand, the influence of electrochemical hydrogen charging before heating on the phase formation was studied.

$Mg_{63}Y_7Ni_{30}$ ribbons were produced by melt spinning to obtain a nanocrystalline - amorphous starting material. The galvanostatic hydrogen charging was performed with $-1\text{mA}/\text{cm}^2$ and a hydrogen concentration $[H]$ of $0.3 < [H] < 1.4$ wt% was determined by hot extraction before and after

heating. The crystallization was observed by means of a PAAR high temperature chamber XRK900 and hydrogen atmosphere or high-vacuum.

The crystallization of the nanocrystalline - amorphous material starts at $T > 150^\circ\text{C}$ for ground material and at $T = 130^\circ\text{C}$ for 4h ball-milled ribbons. The phases Mg_2Ni , pure magnesium and the metastable phase Mg_6Ni were formed simultaneously. It is assumed, that Y is dissolved in Mg_2Ni or remains in the residual amorphous matrix up to 300°C . Y - phases were observed only at about 300°C . That means, in hydrogen atmosphere a YH_3 phase is formed, whereas for annealing without hydrogen atmosphere an oxide is obtained.

Figure 1 shows a crystallized sample after thermal treatment under high-vacuum up to 250°C in comparison to the crystallization under 0.5 MPa hydrogen. The X-ray patterns are very similar. Obviously, the gas-solid reaction is inhibited by a surface passivation. The hydrogen content after heat treatment is only 0.05 wt% in this case.

Figure 2 shows the phase composition at 230°C and about 70 kPa hydrogen pressure for different electrochemically charged samples. With increasing temperature and hydrogen concentration obtained by electrochemical charging the formation of Mg_6Ni is inhibited in favour of pure magnesium. Above 250°C Mg_6Ni is decomposed in all cases. Furthermore, the hydrogen is found in the Mg_2Ni phase. That means, a solid solution Mg_2NiH_x ($0.2 < x < 0.3$) is formed.

For samples having a hydrogen concentration of 1.4 wt% the crystallization of Mg_2NiH_x ($0.2 < x < 0.3$) and

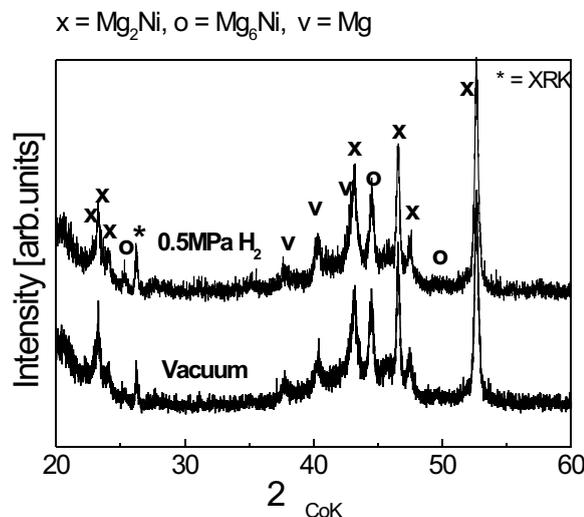


Figure 1: Crystallization of $Mg_{63}Y_7Ni_{30}$ after annealing to 250°C : $x = Mg_2Ni$, $o = Mg_6Ni$, $v = Mg$

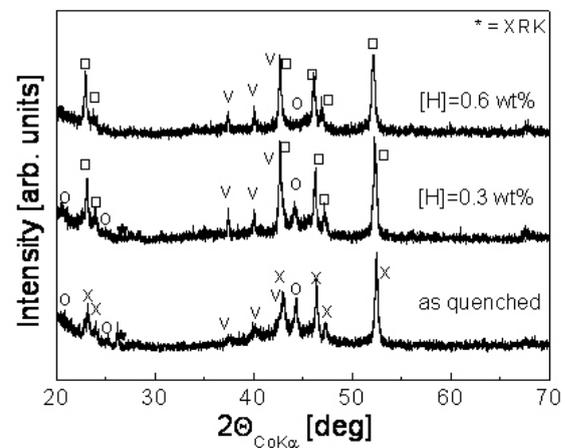


Figure 2: Phase composition at 230°C for different charged samples: $x = Mg_2Ni$, $o = Mg_6Ni$, $v = Mg$, $\square = Mg_2NiH_x$ ($0.2 < x < 0.3$)

Mg₆Ni is observed only at 230°C. At 250°C the complex compound Mg₂NiH₄ is formed (Figure 3). Mg₂NiH₄ shows the high temperature modification with fcc structure. At equilibrium conditions this phase is formed only at 300°C. Furthermore, a small amount of Ni₂Y₃ or NiY is assumed above 240°C. Mg₂NiH₄ transforms reversibly into Mg₂Ni at 300°C under desorption conditions. At cooling a gas-solid reaction is detected with the hydrogen atmosphere in the chamber and the Mg₂NiH₄ compound is formed again. At room temperature the rhombic structure was found.

Future investigations will deal with the influence of higher current density on the electrochemical charging and the crystallization. Furthermore, the possibility of a gas-solid reaction with hydrogen should be proved. The role of yttrium on the hydrogen absorption has to be clarified.

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T9 - P162

IN-SITU INVESTIGATION OF COSN₂ AS CATALYST FOR SELECTIVE HYDROGENATION OF ACROLEIN BY POWDER DIFFRACTION

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The last few years has seen an increasing demand of high temperature powder diffraction experiments under controlled atmosphere [1-4]. Such a setup combined with a gas mixing unit and an online chemical analysis of the product gas stream is suitable for investigations in the field of heterogeneous catalysis.

A quartz glass capillary with 1 mm outer, 0.5 mm inner diameter with a total length of 13 cm is built in a graphite rod of an electric resistance heater and connected by Swagelok fittings with Teflon ferrules to gas pipes. Into these gas pipes two thermocouples are embedded to control the temperature in front and behind of the sample. Additionally, these thermocouples are also fixing the sample in the capillary. First experiments were performed onto the selective hydrogenation of acrolein [5] in the temperature range up to 300°C using molecular hydrogen and CoSn₂ as non-supported catalyst prepared by solid-state chemistry.

The catalyst embankment has an initial high of approx. 9 mm and was compressed by the gas stream to approx. 6 mm, therefore a pressure loss of 8 bar results. The gas stream was 2-5 l/h. The experiments were performed in following order: 1. with N₂ atmosphere, 2. with H₂, 3. with N₂ for hydrogen desorption, 4. with an acrolein /hydrogen mixture (molar ratio 1:20) and again with N₂ for desorption

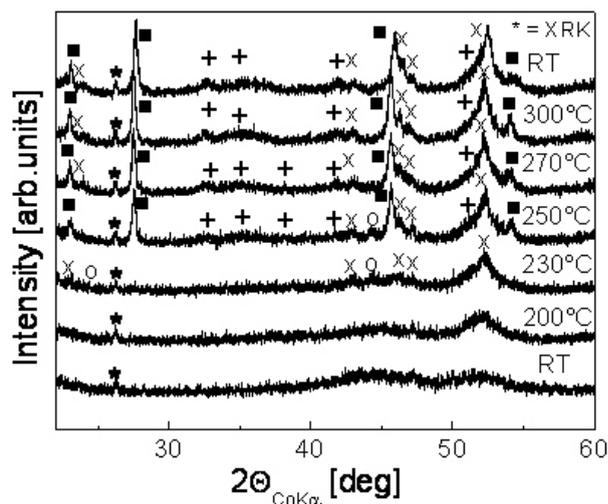


Figure 3. Crystallization of Mg₆₃Y₇Ni₃₀ after electrochemical charging with 1.4 wt% hydrogen: ■ - Mg₂NiH₄, + = Ni₂Y₃ or NiY (?)

- [4] M. Savyak, S. Hirnyj, H.-D. Bauer, M. Uhlemann, J. Eckert, L. Schultz, A. Gebert, J. Alloys Comp. 364 (2004) 229.

(data point 100 °C of the acrolein/hydrogen series). Additionally, for comparison the sample was measured ex-situ with a standard furnace.

CoSn₂ crystallizes in the space group nr.140; I4/mcm; a = 6,361; c = 5,452 Å [6]. The data evaluation is performed by crystal structure analysis, using the Rietveld method. Fig. 1 displays minor differences in the lattice parameter a between ex-situ and in-situ data using N₂ atmosphere. Obvious are the differences in lattice parameter between N₂ and H₂ atmosphere especially at room temperature. The CoSn₂ lattice expand by adsorption of H₂, desorption experiments show that these process is irreversible and also not influence by acrolein in the H₂ gas stream. Beside thermal expansion, no effect of the atmosphere onto the lattice parameter c is observed.

The decrease of FWHM during the experiment gives evidence for a crystal growth in the temperature range between 200 and 300°C at the first heating. This result was testified in the ex-situ experiments.

Acknowledgement

We gratefully acknowledge the financial support of the BMBF (grant nr. 05KS1RDA/9) and of the DFG (CL 168/3-2).



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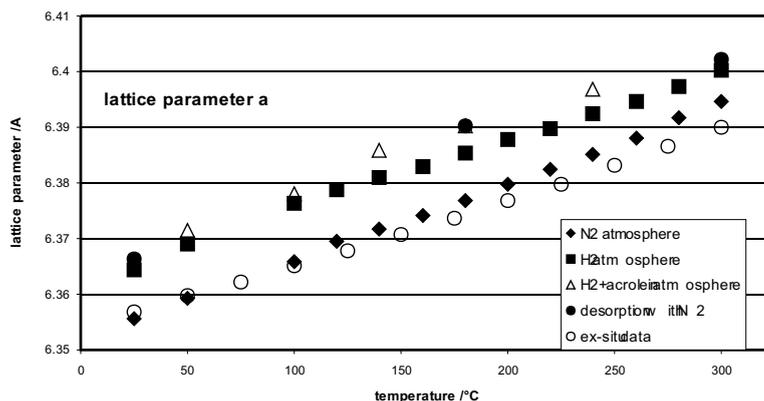


Fig. 1: Influence of the gas atmosphere onto the lattice parameter a.

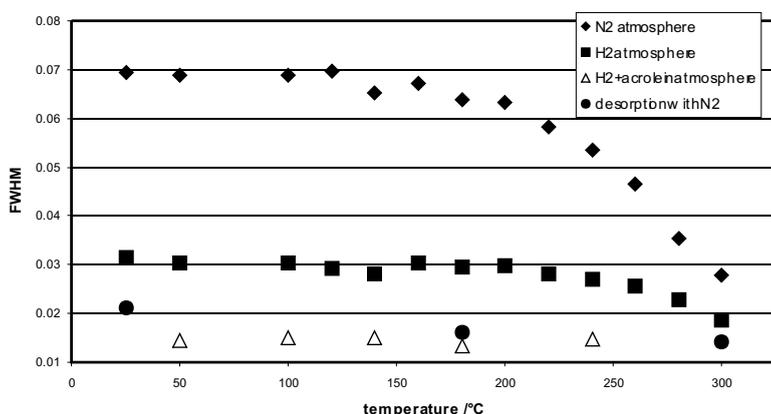


Fig.2: Decrease of FWHM parameter of reflections during heating

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T9 - P163

IN-SITU INVESTIGATION OF LiMn_2O_4 AS CATHODE MATERIAL IN SECONDARY LITHIUM ION BATTERIES BY POWDER DIFFRACTION

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In the past 15 years the field of secondary lithium ion batteries gained a dramatic increase in interest due to the increasing mobility of our society. Higher specific energy densities as well as higher cell voltages are the desirable key features while costs, capacity fading and possible hazards should diminish. LiMn_2O_4 is well known for the potential use in secondary lithium ion batteries [1, 2]. Its behaviour during cycling strongly depends on doping and coating of the cathode material and on the first charge cycle. This work will demonstrate that in-situ powder diffraction is a powerful tool to investigate such modification of the material during cycling [3, 4]. LiMn_2O_4 synthesised by solid state reaction is compared with commercial produced one, provided by Kerr & McGee. The use of synchrotron radiation and fast detector systems [5] is inevitable for such experiments. The measurements were performed at

beamline B2 HASYLAB Germany [6] and investigate the first charge cycle. 33 (and 47 for the Kerr & McGee sample respectively) diffraction patterns for the first charge cycle, equivalent to lithium deintercalation, were collected. For cycling a VMP multi potentiogalvanostatic device (VMP 60, Perkin-Elmer) was used.

In contrast to pure LiMn_2O_4 , which exhibit in the range of 3.8 up to 4.4V two well defined plateaus, the commercial product shows a sloped curve and only 0.35 instead of 0.19 lithium are extracted from the substance, so the capacity is smaller. In general, a plateau in these plots is indicating a two phase region.

LiMn_2O_4 crystallizes in the space group $\text{Fd-}3\text{m}$ No.227 with $a = 8.24 \text{ \AA}$. The data evaluation is performed with the program package FULLPROF-Suite. The first sample shows an unusual peak broadening in the range of $x = 0.65$

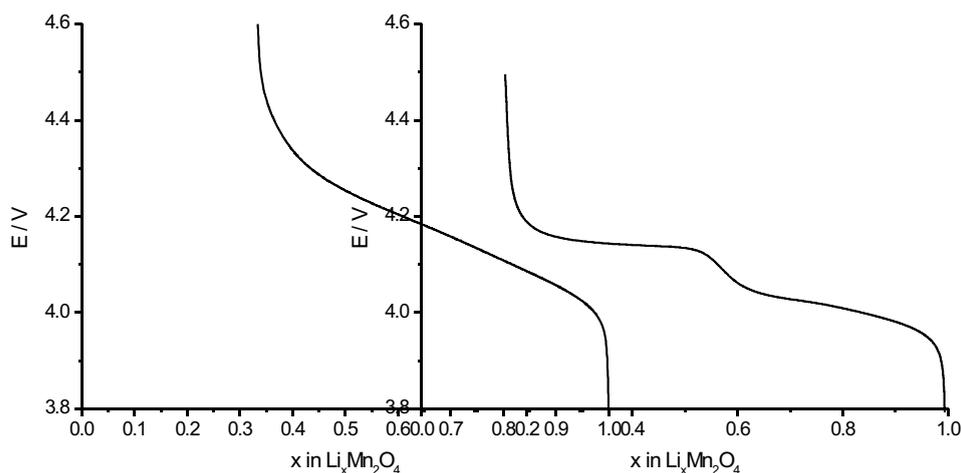


Fig.1: First charge cycle of LiMn_2O_4 as received by Kerr & McGee and by synthesised by solid state

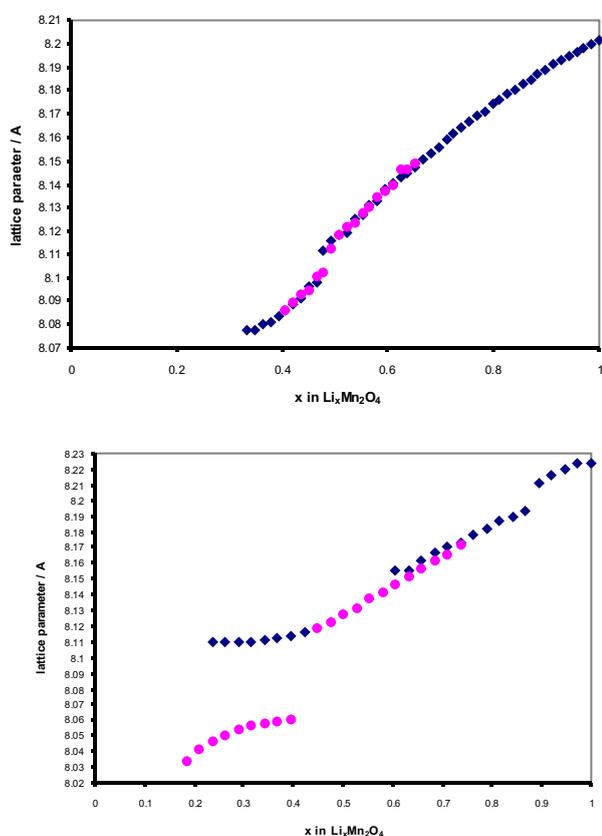


Fig.2: Lattice parameter during the first charge cycle of LiMn_2O_4 as recieved by Kerr & McGee and by synthesised by solid state reaction

down to 0.4 in $\text{Li}_x\text{Mn}_2\text{O}_4$, which is due to a second spinell phase with a slightly different lattice parameter. This effect is also observed in the unmodified $\text{Li}_x\text{Mn}_2\text{O}_4$ in the range of $x = 0.73$ to 0.6. In this region of deintercalation two phases coexist and counteract with respect to their phase amount. In the region of $x = 0.4$ to 0.24 two coexisting phase were observed again, but here the differences in the lattice parameters are much more pronounced [6, 7].

The appearance of the second two-phase region could not be observed by the sample provided by Kerr & McGee,

probably it is suppressed by coating and doping of the substance. Additionally the changes of lattice parameters during cycling are slightly smaller compared with pure $\text{Li}_x\text{Mn}_2\text{O}_4$.

So powder diffraction technique using synchrotron radiation is a sophisticated method for phase and crystal structure analysis during cycling of battery cells. It leads powder diffraction data sets suitable for Rietveld refinements. Due to the high time resolution and the high instrumental resolution of the set-up a well defined picture of the battery system can be concluded. This allows the tracking of internal processes during cycling with the advantages of in situ investigations.

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T9 - P164

PHASE EQUILIBRIUM IN THE YAG-YAP SYSTEM UNDER PRESSURE

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Transparent yttrium-aluminum garnet (YAG) nanometric ceramics can be prepared by sintering YAG nanopowders under pressure. However, under pressure YAG decomposes into yttrium-aluminum perovskite (YAP) and Al₂O₃ at the temperatures considerable lower than under ambient pressure. That effect imposes limits on the sintering conditions and time. In order to determine the pressure-temperature conditions at which YAG ceramics can be safely obtained we have conducted a systematic study of the pressure effect on the decomposition temperature of YAG.

The experiments were conducted *in-situ* in the Hamburg Synchrotron Radiation Laboratory HASYLAB using the MAX-80 multi-anvil HP-HT apparatus. The instrument works in the energy-resolved geometry: the incoming beam is white, the diffraction angle is fixed and the pattern is collected with the solid-state detector and the multi-channel analyzer.

At ambient pressure YAG is stable well above 1500°C. At each pressure above 2GPa there exist a narrow (approx. 100deg) range of temperatures where the decomposition speed increases dramatically and above which YAG entirely decomposes into YAP and Al₂O₃ within seconds. The mid-points of those ranges are plotted in Figure 1 against the pressure. As can be seen the most pronounced changes occur within 2-4 GPa pressure range. At higher pressures the characteristic decomposition temperature levels-out at approx 650°C.

Our result is in qualitative agreement with an earlier study on the decomposition of yttrium-iron garnets [1.]

The process dynamics and the reasons for the decrease of the stability of YAG under pressure will be discussed.

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T9 - P165

POWDER DIFFRACTION STUDY OF THERMAL EXPANSION AND CRYSTAL STRUCTURE OF THE AURIVILLIUS PHASES IN THE Bi₄Ti₃O₁₂-BiFeO₃ SYSTEM

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The Aurivillius family of layered Bi-containing oxides is well known for its ferroelectric properties. Usually their crystal structure is described as a combination or intergrowth of (Bi₂O₂)²⁺ layers and (A_{n-1}B_nO_{3n+3})²⁻ perovskite-like blocks, where A is a twelve co-ordinated cation e.g. Na, K, Ca, Sr, Ba, Pb, Bi, etc. and B is an octahedral cation such as Fe, Ti, Nb, Ta, Cr, etc.

In the Bi₄Ti₃O₁₂ - BiFeO₃ system the compounds with general chemical formula Bi₂Bi_{n-1}(Ti,Fe)_nO_{3n+3}, n = 3, 3.5, 4, 4.5, 5, 6, 8 synthesised by solid state reaction are noted in [1]. The crystal structures of the compounds with n = 3, 3.5, 4 are determined in orthorhombic system in [2], [3], [4] respectively. The structure of Bi₄Ti₃O₁₂ (n=3) is refined by Rietveld method in orthorhombic space group B2cb at 25, 500 and 650 °C and in tetragonal space group I4/mmm at 800 °C [5]. For Bi₅Ti₃FeO₁₅ (n = 4) the polymorph phase transition from polar orthorhombic A2₁am space group to

tetragonal I4/mmm is studied in details by Rietveld method using PND data [6]. Its transition temperature determined as ~ 730 °C is coincident with Curie temperature corresponded to ferroelectric-paraelectric transition.

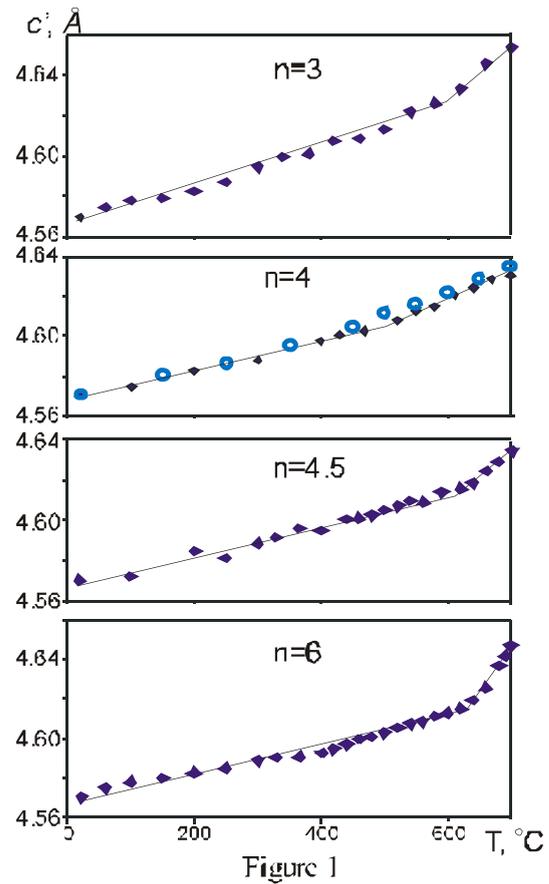
Now we investigate the thermal behaviour of four aurivillius phases with n = 3, 4, 4.5 and 6 using high-temperature X-ray powder diffraction in air (CuK_α -radiation, the temperature range 20-700 °C) and DTA method (20-1300 °C). The temperature dependence of *c* cell parameter counting on a perovskite layer (*c'*) is presented in Fig. 1 along with the data from [6] for n = 4. The dependence is obviously divided into two ranges: the low temperature region with a lower thermal expansion and a high temperature region with a greater expansion. The linear thermal expansion coefficient α_c for HT phase is 3 times larger than that one for LT phase. Since *a* and *b* cell parameters (5.46 ± 0.03 Å) and correspondingly the paired hkl, khl re-

Table 1. Thermal behaviour of aurivillius phases from HTXRD and DTA data. Specific temperature points (°C): (A) the inflection point of c cell parameter vs. temperature; (B) FWHM of paired peaks is equal to that of unique; (C) DTA endothermic effect

	A	B	C
$n=3$	610	660	660
$n=4$	500	640	740
$n=4.5$	600	600	690
$n=6$	620	620	650

flexions are very close to each other in the studied compounds, it is complicated to calculate a and b values correctly. To define the orthorhombic-tetragonal transition point we analyze the FWHM temperature changes for unique and paired reflections. For example for $\text{Bi}_5(\text{Ti,Fe})_4\text{O}_{15}$ ($n=4$) the FWHM of the reflection $hkl:119$ ($I/I_0 = 100\%$) practically does not change under heating: 0.33° at 20°C and 0.31 at 640°C . FWHM of paired reflection 200 and 020 ($I/I_0 = 30\%$) decreases from 0.45° at room temperature up to 0.31 at 640°C . If the orthorhombic structure transfers to tetragonal the FWHM of unique and paired reflections becomes equal. Also a weak endothermic effect is observed on the DTA curve in the range of temperatures $650\text{--}740^\circ\text{C}$ in all studied samples. The Table 1 contains the following specific temperature points: (1) the inflection point of c cell parameter vs. temperature; (2) the temperature point in which the FWHM of unique and paired reflections becomes equal; (3) the DTA endothermic effect. Clearly, that the temperature of DTA effect is always higher than the changes in XRD pattern on heating. It could be caused by a different heating rate.

As far as we are aware, there is only one crystal structural study of Aurivillius phase structure with c parameter 57.6 \AA corresponded to a 6 layer-structure [7]. For $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ we propose the structural model based on 6 layered perovskite blocks. To build up the model the atomic coordinates of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ [4] were used. It was refined in orthorhombic $Fmm2$ space group: $a = 5.474(1)$, $b = 5.495(1)$, $c = 57.60(1) \text{ \AA}$ with Rietica for Rietveld refinement program ($R_p = 10.2$, $R_{wp} = 13.3$, $R_B = 5.6\%$). It was also refined in $A2_1am$ space group but no additional reflections which are compatible with this lower symmetry were observed. Relatively high R-factors are caused probably by the structure defects. The FWHN for reflection of $00l$ type is two-three times larger than that one for other reflections. Perhaps the number of layers in block is not constant in the structure, but the considerable amount of 6-layer phase is present. This structure could also be described in terms of crystal chemistry with oxocentered



anions as an alternation of perovskite blocks and Bi-O layers build up from OBi_4 tetrahedra by sharing edges (Figure 2).

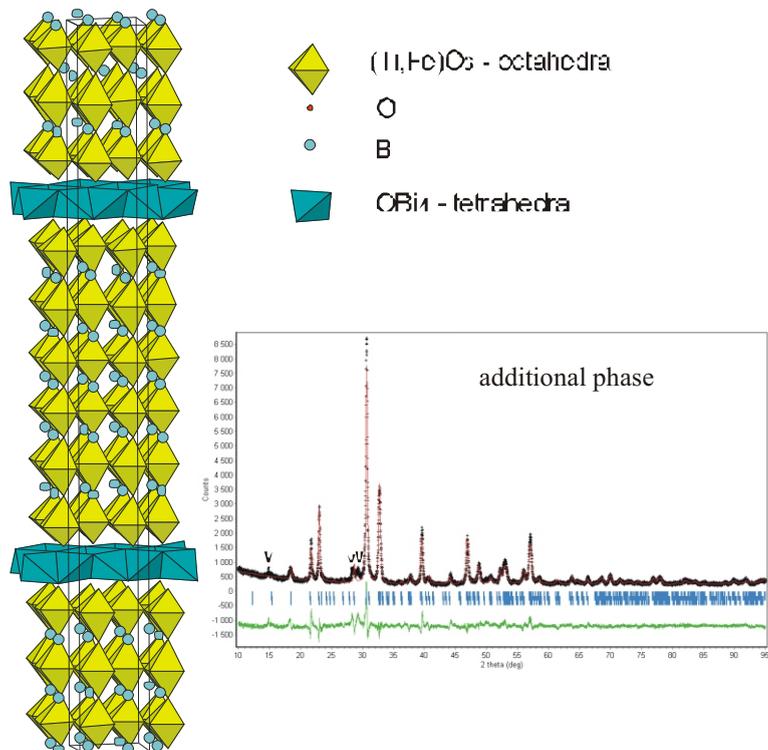


Figure 2. The Crystal structure of $\text{Bi}_7\text{Ti}_3\text{Fe}_3\text{O}_{21}$ and the Rietveld data plot.



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T9 - P166

PREPARATION AND X-RAY POWDER DIFFRACTION STUDIES OF CRYSTAL STRUCTURE AND THERMAL BEHAVIOUR OF (Na,K)-TRIBORATES

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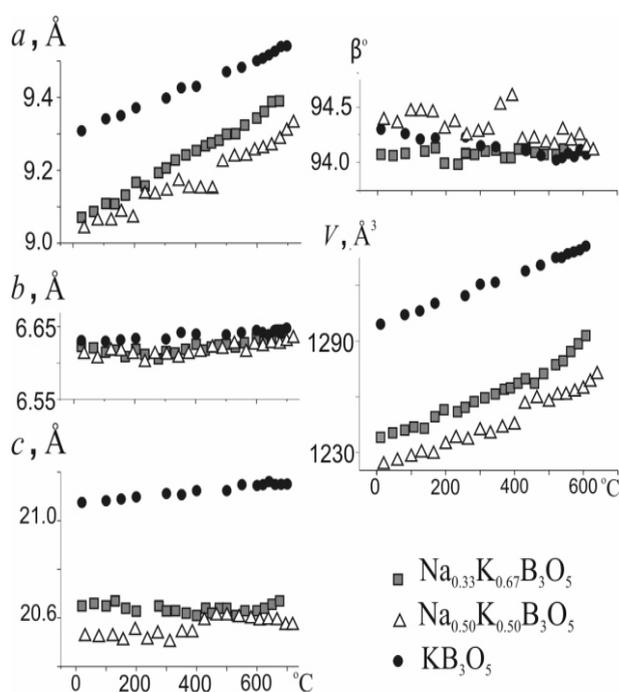
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Recently, the crystal chemistry of borates has been re-investigated because the borate compounds have received great attention due to their non-linear optical, piezoelectric, luminescent and other useful properties. In view of examining new anhydrous borates with interesting physical properties NaB₃O₅-KB₃O₅ pseudobinary system has been investigated.

Phase relations in the NaB₃O₅-KB₃O₅ system were studied *in situ* using high-temperature X-ray powder diffraction and DSC as well as annealing and quenching methods. The samples under investigation were prepared by glass crystallisation as well as solid state reaction methods. Below 650 °C in the KB₃O₅-enriched part of the system the solutions of Na_{1-x}K_xB₃O₅ (0.5 < x < 1) exist; in the NaB₃O₅-enriched part two phases -NaB₃O₅ and Na_{1-x}K_xB₃O₅ (x < 0.5) co-exist [1]. Above 650 – 670 °C Na_{1-x}K_xB₃O₅ solid solutions in the range of x = 0.75-1.0 decompose to K₅B₁₉O₃₁, K₂B₄O₇ and Na_{1-x}K_xB₃O₅ solid solution enriched by NaB₃O₅. The Na_{1-x}K_xB₃O₅ solid solutions in the range of x = 0.5-0.67 melt according to the peritectic reaction Na_{1-x}K_xB₃O₅ = K₅B₁₉O₃₁ + Liquid.

The crystal structure of E₂Ä₃Î₅ [2] was determined in the monoclinic P2₁/c space group using single crystal diffraction data. It contains three-dimensional framework of triborate groups. There are three structurally independent positions for K atoms in channels of the B-O anion framework. The order-disorder distribution of K and Na atoms in these positions has been investigated in series of Na_{1-x}K_xB₃O₅ solid solutions where 0.5 < x < 1. Crystal structures of three Na_{1-x}K_xB₃O₅ solid solutions (x = 0.8, 0.75 and 0.55) were refined from powder data using Rietica program. The samples were biphasic. For example, the sample with 80 mol. % KB₃O₅ (R_p = 4.2, R_{wp} = 5.3, R_B = 2.2 %) contained mainly Na_{1-x}K_xB₃O₅ (about 95 mol. %) a = 9.1539(5), b = 6.6295(5), c = 20.742(1) Å, â = 94.07(1)° and traces of K₅B₁₉O₃₁ (about 5 mol. %). Two positions were occupied by K atoms and the third, the smallest one,



was occupied by K and Na atoms. The sample with 55 mol. % KB₃O₅ (R_p = 5.6, R_{wp} = 7.1, R_B = 2.9 %) contained Na_{1-x}K_xB₃O₅ (about 97 mol. %) a = 9.0561(5), b = 6.6172(5), c = 20.584(1) Å, â = 94.22(1)° and traces of -NaB₃O₅ (about 3 mol. %). In this solid solution the smallest cationic position was occupied by Na atoms only. Thus, we can propose that the composition of Na_{0.33}K_{0.67}B₃O₅ is really a new NaK₂B₉O₁₅ compound in which K and Na atoms are distributed ordered: two positions are occupied by K atoms and the smallest - by Na ones. The coordination number and the average <(Na,K)-O> bond length of the smallest polyhedron decrease as K atoms are replaced by Na atoms: the <(Na,K)-O> bond length decreases from 2.815 Å for KO₇

polyhedron in KB_3O_5 structure up to 2.49 Å for NaO_6 polyhedron of $\text{Na}(\text{K}_{1.7}\text{Na}_{0.23})\text{B}_9\text{O}_{15}$.

Thermal expansion of $\text{Na}_{1-x}\text{K}_x\text{B}_3\text{O}_5$ solid solutions is similar to all studied samples. It has sharply anisotropic character: for example, the main coefficients of expansion for $\text{Na}_{0.33}\text{K}_{0.67}\text{B}_3\text{O}_5$ are $\alpha_{11} = 52$, $\alpha_{22} = 3$, $\alpha_{33} = 0.5 \times 10^{-6} \text{ C}^{-1}$, $\alpha_{11} = (\alpha_{22} \alpha_{33}) = 2^1$. Thermal dependencies for unit-cell parameters are shown for the solid solutions $\text{Na}_{1-x}\text{K}_x\text{B}_3\text{O}_5$ ($x = 0.5, 0.67$) in comparison to KB_3O_5 in the Figure. Minimum expansion $\alpha_{22} = \alpha_b$ is directed along infinite channels of framework structure.

T9 - P167

STRUCTURAL CHARACTERISATION OF HIGH-TEMPERATURE K-EXCHANGED SODALITE

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The extended use of IFR nuclear plants of the last generation must be accompanied by in-depth studies about waste management and inertisation prior to storage in repository sites, with the aim of reducing the environmental impact of nuclear waste. Electro-refining cells produce, as a by-product, highly soluble alkaline and alkaline-earth chlorides that must be trapped in some inert matrix, temperature and transmutation resistant. Zeolites and framework materials are potentially a good matrix for trapping such ions within their channels. Na-sodalite ($\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}\text{Cl}_2$) was synthesised under hydrothermal conditions from a natural kaolinite in a 4M solution of sodium hydroxide, at 80°C. Kaolinite is a promising starting material, due to its Si:Al=1:1 ratio and to its low costs. The so-obtained Na-sodalite was exchanged with K at high temperature via a solid state reaction with excess KCl. The reaction was performed ex-situ at 800 °C by mixing it with an excess of KCl corresponding to 1:10 in weight, and pressing in an uniaxial press. The resulting pellet was heated in an oven at 800 °C for 12 hours and then quenched rapidly. The K-exchanged sodalite was then analysed by X-ray powder diffraction in order to evaluate its cell parameter and to fully refine its structure. The results, concerning cell parameters, can be found in the figure (open squares): about 60% of the ions in the channel are potassium. The line in the figure was obtained by interpolation of the two theoretical values of pure Na-sodalite and pure K-sodalite: from this line, the K content of sodalite can be inferred. The relationship between cell parameter and composition was confirmed by chemical analyses performed by means of atomic absorption experiments and by the refinement of the occupancy of Na-site, which showed about 60 % substitution with K.

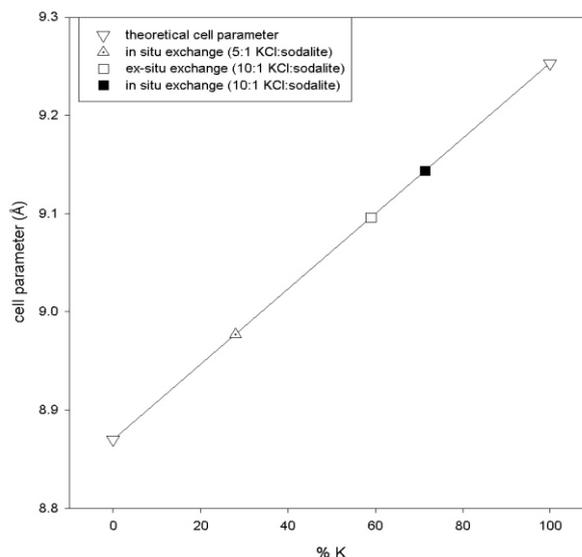
The same exchange reaction was performed in-situ in a hot-chamber installed on the diffractometer, with two different sodalite : KCl proportions (5:1 and 10:1). The exchange reaction was followed in-situ with the evaluation of the change on the cell parameter as a function of time. The final cell parameter is diagrammed in the figure (triangle up

This research has been supported by RFBR (project 02-03-32842).

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and black square for the 5:1 and 10:1 mixtures respectively); the higher the excess of KCl (melting point 772 °C) in the reaction, the higher the exchange kinetics in the sample, because a substantial part of KCl sublimates at high temperature. Again, the structural refinement showed a good agreement between the composition evaluated from the cell parameter and the K occupancy of the Na site. The cell parameter of the K-exchanged sodalite proved then to be a good indicator of the content of potassium in the structure, and therefore of the degree of advancement of the exchange reaction.

Further analyses are being carried out to test the possibility of using the products of this exchange reaction as actual inertisation matrices for different radiogenic ions.





T9 - P168

NEUTRON DIFFRACTION STUDY CRYSTAL STRUCTURES OF KAlO_2 AND Cs_3PO_4 IN WIDE RANGE OF TEMPERATURES

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Solid orthophosphate ceria and potassium aluminate electrolytes are desirable materials for industrial applications. It is well known that the main factor determining an electrical property of the solid electrolytes is their crystal structure. Therefore, cation conductivity and crystal structure of KAlO_2 and Cs_3PO_4 has been studied in present work. Conductivity dependences on temperature in Arrhenius plots – $\lg(\sigma)$ -vs $1/T$ are shown in Figure 1 and 2.

It is seen that behavior of conductivity is very similar in these compositions. In initial KAlO_2 and Cs_3PO_4 samples conductivity jump are observed in high temperature region and the values of activation energy are decrease. The conductivities are significantly increased as the doped element content increases, end bending points are on Arrhenius plots at some temperatures. To understand the reason of such behavior of conductivity neutron-diffraction experiments in a wide range of temperatures were carried out. Be-

cause of samples chemical activity and their hygroscopicity and to prevent their contacts with air all samples were placed in quartz-closed ampoules. Therefore, there is a wide diffused halo of amorphous quartz on neutron diffraction patterns. The neutron diffraction patterns obtained for KAlO_2 and Cs_3PO_4 (fig. 3,4) show that the samples were monophasic. The Rietveld analysis of the diffraction pattern revealed that the KAlO_2 and Cs_3PO_4 crystallize in the orthorhombic space groups, *Pbca* for KAlO_2 ($a = 5.4446(9)$ Å, $b = 10.931(1)$ Å, $c = 15.458(2)$ Å) and *Pmmm* for Cs_3PO_4 ($a = 14.590(5)$ Å, $b = 10.219(3)$ Å, $c = 7.780(2)$ Å). Analyze also showed that KAlO_2 structure has the tetrahedra AlO_4 forming three-dimensional framework with full connectivity. On the contrary in Cs_3PO_4 the tetrahedra PO_4 are separated spatially. We found that Cs_3PO_4 and KAlO_2 exhibits structural phase transition at T

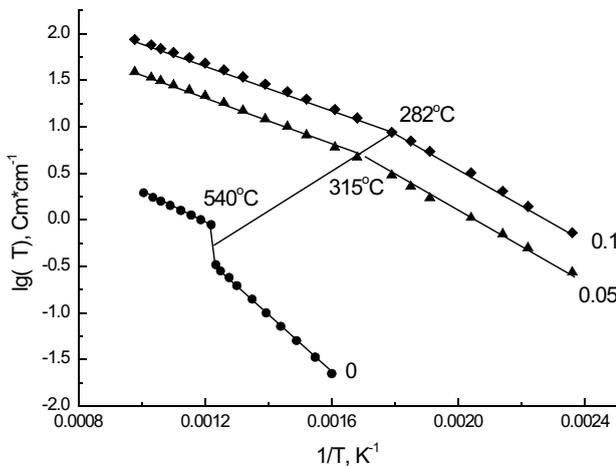


Fig.1. Arrhenius plots $\text{K}_{1-x}\text{Al}_{1-x}\text{Ti}_x\text{O}_2$.

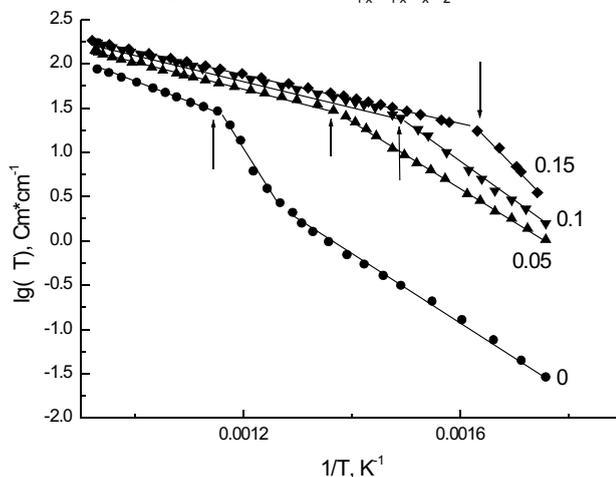


Fig.2. Arrhenius plots $\text{Cs}_{3-2x}\text{Ba}_x\text{PO}_4$.

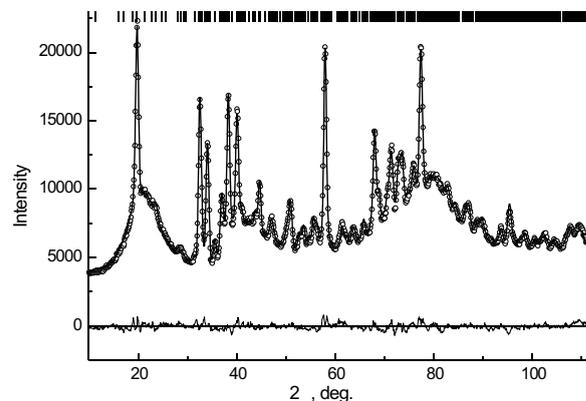


Fig.3. Neutron diffraction pattern of KAlO_2 at room temperature.

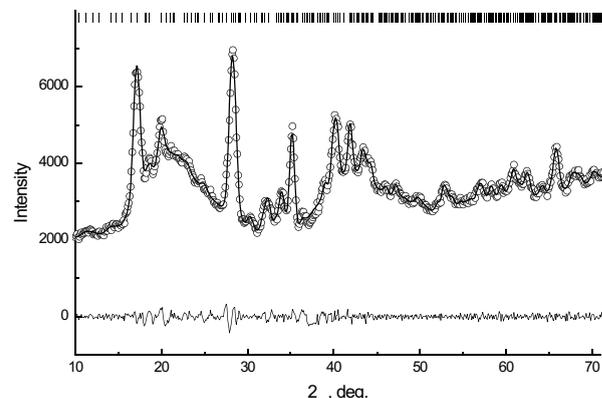
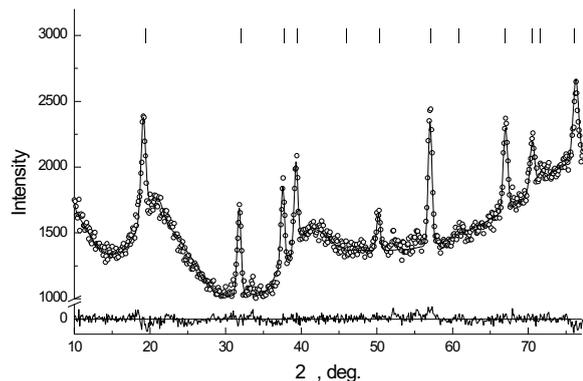
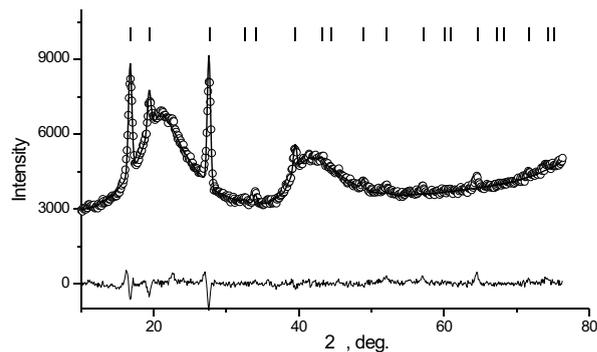


Fig.4. Neutron diffraction pattern of Cs_3PO_4 at room temperature.


 Fig.5. Neutron diffraction pattern of KAlO_2 at $T=575^\circ\text{C}$.

 Fig.6. Neutron diffraction pattern of Cs_3PO_4 at 600°C .

~ 790 K and ~ 813 K, correspondingly (fig. 5,6), followed by the thermal conductivity jump (fig. 1,2).

Using high temperature structure -cristobalite study results [111] it has been showed that at $T > 540^\circ\text{C}$ the aluminum, potassium and oxygen atoms occupy, respectively, the special equivalent positions $8a$, $8b$ and $16c$ in the space group $Fd\bar{3}m$. It is an "ideal" model that gives a bad experiment description. Disordered models give good accordance with experiments. In the first model the oxygen atoms do not lie on well-defined positions, but the Al-O bond precesses about its average orientation so that the oxygen atoms lie on an annulus of fixed radius (~ 0.5 Å). In the second model the oxygen atoms are placed in the $96h$ sites, with partial occupancy of $1/6$. We cannot prefer any of these models from our experimental data. More precise example is given in Fig. 5.

In high temperature phase orientationally disordered phosphate ions occupy an FCC lattice, and the sodium cations occupy all tetrahedral and octahedral interstices (neutron diffraction patterns show at fig.6).

Crystal structures of KAlO_2 and Cs_3PO_4 are cubic at room temperature because of doping them by titanium and barium, respectively. However these cubic structures are disordered as for according high temperature phases, but this disordering is static and dynamic at high temperature. There is an increase of disordering degree of the $\text{K}_{1-x}\text{Al}_{2-x}\text{Ti}_x\text{O}_2$ ($x=0.2$) sample as the temperature increases and Debay-Waller factor significant increases.

Because of crystal structure features it was suggested the conductivity mechanism at high temperatures in so called superionic state. As it was mentioned earlier there are rigid tetrahedra PO_4 groups in orthophosfat cesium which are saved their form in whole temperature region. However, large Debye -Waller factors in superionic state suggest dynamic disordering. These facts mean group motion as a whole. Such model was suggested for isostructural compound Na_3PO_4 based on complex study of structural state at high temperatures using different methods. Inelastic neutron scattering experiments showed rotor motion of these complexes. It's the model suggests strong coupling between the reorientation of anions and the mobility of cations – the "paddle-wheel mechanism". The cubic structure appears at room temperature at doping of compounds that is why such correlated tetrahedra PO_4 rotation and cesium

ions diffusion appears at lower temperature. This process is illustrated by bending point on Arrhenius plots; bending point temperature decreases with barium concentration (Fig.2).

Additional conducting channels appear at phase transition into cubic phase in KAlO_2 lattice. At the same time such "paddle-wheel mechanism" occurs in KAlO_2 . Because of tetrahedrals link by oxygen atoms there are correlating AlO_4 vibrations and motion of K cations with increasing temperature. This correlation is confirmed by sharp activation energy decreasing at doping with titanium (Fig.1). And the bending point temperature decreases as the Ti concentration increase.

Work supported by State Scientific Research Program "Neutron Investigations of Condensed Matter" (State control No. 40.012.1.1.11.50) and the basic research program of the Department of Physical Sciences of the Russian Academy of Sciences "Neutron studies of the substance structure and fundamental properties of matter".

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T9 - P169

IN-SITU NEUTRON DIFFRACTION STUDY OF α -BISMUTH MOLYBDATE

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The room temperature HRPD (High Resolution Powder Diffraction) and *in-situ* MRPD (Medium Resolution Powder Diffraction) have been performed to study the unit cell structure changes in an α -Bi₂Mo₃O₁₂ catalyst under ambient and reaction conditions. The unit cell parameters (a, b, c and β), inter-atomic distances and temperature factors have been obtained after refining the HRPD and MRPD diffractograms using the Rietveld method and the RIETICA software. The unit cell parameters of α -Bi₂Mo₃O₁₂, resulting from the Rietveld refinement of the room temperature HRPD diffractogram, are a = 7.1517(38) Å, b = 11.5263 (52) Å, c = 11.9568 (66) Å and β =

115.2733° (43). The refinement of *in-situ* MRPD diffractograms shows that the unit cell expanded anisotropically, where the expansion in **b** direction is faster than in the other directions. It is also shown that some oxygen atoms, namely O1, O4, O5, O11 and O12, are more sensitive toward the *in-situ* condition. Oxygen atoms No 1, 11, and 12 are lying on the interface between two bismuth molybdate layers in the unit cell and bounded solely to molybdenum atom. These oxygen atoms are suspected of being the source of the oxidising oxygen responsible for the selective oxidation of propylene to acrolein.

T9 - P170

NEUTRON DIFFRACTION STUDIES OF TEMPERATURE INDUCED PHASE TRANSITIONS IN Rb₂KFeF₆ ELPASOLITE

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Rb₂KFeF₆ fluoride belongs to compounds family with general chemical formula A₂BMF₆ (A, B – monovalent cations, M – trivalent cation). The space group of their cubic prototype is Fm3m (Z = 4). In this system two kinds of non-equivalent octahedral groups (BF₆ and MF₆) alternate along the three four-fold axes. The region of cubic lattice stability depends on tolerance factor [1]. Fm3m symmetry is usually observed in the wide temperature region at the 0.88 < t < 1.0. Distortion of the octahedral group takes place at the t < 0.88. This fact leads to crystal symmetry reduction. The structure of crystals with low M³⁺ (M = Cr, Ga, Fe) radius is still poorly known. These compounds usually demonstrate ferroelastic phase transition which corresponds considerable high changing in entropy DS. We

studied structure of the Rb₂KFeF₆ (t = 0.885; DS/R = 1.88) at the wide temperature region. Fig. 1 shows neutron diffraction pattern and the result of Rietveld refinement at the room temperature.

We performed refinements with fluorine atoms in 96k position and Rb – in different positions according to group-theory analysis [2] of distortions of initial Fm3m structure caused by octahedron or/and polar atoms displacements. Refinement of the low temperature phase in the frame of Pmnn space group was also performed.

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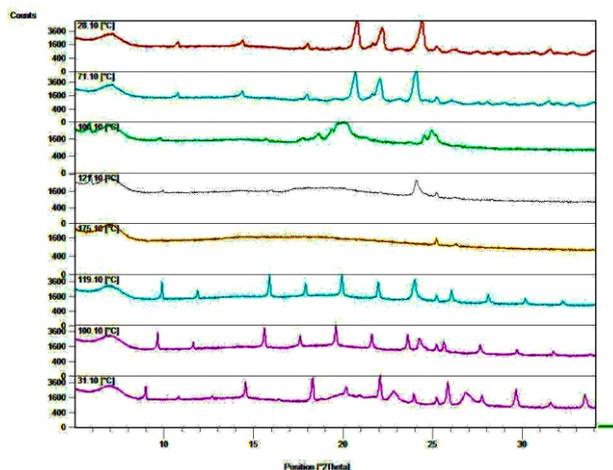
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T9 - P171

THE POLYMORPHS OF *N*-OCTADECYLAMMONIUM CHLORIDE - A VARIABLE-TEMPERATURE POWDER DIFFRACTION STUDY

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n-Alkylammonium halides ($n\text{-C}_n\text{H}_{2n+1}\text{NH}_3^+\text{X}^-$) are used as surfactants, lubricants, and as models for biological membranes. A spectrum of intermolecular interactions are present in the crystals, ranging from van der Waals interactions between the hydrocarbon chains to ionic and hydrogen bonding interactions in the polar layer. The molecules pack in alternating polar and hydrocarbon layers. Long-chain *n*-alkylammonium halides exhibit polymorphism at room temperature and a complex sequence of solid-solid phase transitions at higher temperatures. The polymorphs of the *n*-alkylammonium chlorides, with alkyl chain lengths up to 18 carbon atoms, were studied by powder and single crystal X-ray diffraction and by thermal analysis techniques. All members of this series exhibit polymorphism. The crystal forms can be classified according to their long spacings as determined by powder diffraction. The *i* form has the smallest long spacing and the *k* form the largest. The crystal structures of the *i* and *k* forms of *n*-octadecylammonium chloride, $\text{C}_{18}\text{H}_{37}\text{NH}_3^+\text{Cl}^-$, were determined by powder and single crystal X-ray diffraction methods. In the *i* form the molecular chains are in the all-*trans* conformation and interdigitated whilst in the *k* form the chains are non-interdigitated and not completely extended, exhibiting a kink between the second and third carbon atoms. Hydrogen bonding interactions are present between the ammonium groups and chloride anions in the ionic layers. The transition sequences between these forms



and the high temperature phases could be determined by thermal analysis (DSC) and a phase sequence diagram constructed. Variable-temperature powder diffraction studies confirmed the transition sequences and proved that the form consistently crystallizes from the melt.

T9 - P172

PHASE TRANSITION TRIGGERED BY SUBSTITUTION IN MONAZITE-TYPE LaVO_4

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Vanadates REVO_4 of the rare-earth elements crystallize in the tetragonal zircon-type structure, except with lanthanum for which the monoclinic monazite-type structure is preferred. However, for certain elements metastable phases of the respective other structure type have been observed. We have studied the substitution series $\text{La}_{1-x}\text{Ce}_x\text{VO}_4$ and $\text{La}_{1-x}\text{Nd}_x\text{VO}_4$. Particular emphasis was put on those phases where the structure changes from monazite to zircon type.

Furtheron the temperature-dependent stability of these particular samples was investigated. High-resolution powder diffraction methods using an image-plate based Guinier-camera had to be used to clearly resolve the pattern of the tetragonal phase along with the quite complicated pattern of the monoclinic phase in two-phase samples.



T9 - P173

X – RAY POWDER DIFFRACTION STUDY OF LEUCITE CRYSTALLISATION

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Leucite based materials are being a subject of an extensive scientific interest in recent years, especially in a field of dental prosthesis. Presence of leucite (KAlSi₂O₆), exhibiting high values of a thermal expansion coefficient, in a porcelain matrix enables its fusion to metal reinforcement. In addition thanks to its phase-transition behaviour leucite could potentially toughen leucite-glass (porcelain) systems and so lead to dental materials having high fracture toughness.

As the amount, average crystal size and structure of the leucite phase directly affect thermal and mechanical properties of the final composite material; suitable technology of its preparation is necessary to be developed.

A new preparation procedure of leucite based on its crystallisation from an amorphous precursor was studied. The precursor was synthesized from a gel containing alu-

minium, amorphous silica and potassium hydroxide solution in hydrothermal conditions at 200°C for 2h. Leucite was subsequently prepared by calcinations of obtained powders.

Crystallisation of leucite was monitored at 800, 900 and 1000°C using X-ray powder diffraction analysis. At high temperatures the stable form of leucite is cubic (high leucite), and as it cools below a temperature of about 630°C there is a displacement phase transformation to tetragonal (low leucite). As this transformation is substantial for the toughening mechanism in leucite dental porcelains the process of leucite transformation was studied using X-ray diffractometer equipped with high temperature cell.

Acknowledgements.

This work was supported by GA CR Grant 104/03/0031.

T9 - P174

STRUCTURAL ASPECTS OF THE METAL-INSULATOR TRANSITION IN BaVS₃

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This study presents structural transitions of the one dimensional system BaVS₃ at low temperature by means of high resolution synchrotron powder diffraction. At room temperature the structure is hexagonal (P6₃/mmc) with face sharing VS₆ octahedral chains along the c axis separated by Ba atoms leading to a V-V intrachain distance of 2.808(1) Å and an interchain distance 6.714(1) Å. The hexagonal structure at room temperature becomes orthorhombic (Cmc2₁) at 240K with a V straight chains transformed into uniform zigzag but without significant change in the elec-

tronic properties. At 70K a metal-insulator transition occurs with the appearance of a superstructure which doubles the chain periodicity. The structure refined at 40K revealed a weak monoclinic distortion (= 90.046(1)°) with 4 non-equivalent V sites. A valence bond analysis shows no evidence for charge disproportionation on these sites. However at 5K, the faces of the VS₆ octahedra are stretched (site V1) or compressed (V3) inducing a 0.5e- charge disproportionation between the V1 and V3 sites.

T9 - P175

HIGH PRESSURE STUDIES OF THE LiAlH_4 AND NaAlH_4 SYSTEMS

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Recent targets set by the International Energy Agency and the United States Department of Energy stipulate that hydrogen storage materials for mobile applications should possess at least 5 wt.% reversal capacity at less than 80 C [1]. The aluminohydrides (alanates) present a new class of promising storage materials that are approaching these mobile targets. The Ti-doped NaAlH_4 system first achieved reversibility in 1997 [2], and there has since been considerable research into both its structural [3, 4] and cycling/kinetic properties [5,6]. Although the LiAlH_4 system has not yet achieved reversibility, there has also been renewed interest in its structural features [7,8].

In terms of volumetric efficiency, it is desirable to store as many hydrogen atoms per unit cell as possible, and high isostatic loading offers the ability to investigate the possibility of stabilising such phases. For the NaAlH_4 and LiAlH_4 systems, theoretical VASP calculations predict pressure induced phase transitions at 6.4 GPa and 2.6 GPa respectively [9], which allows up to a 15% reduction in unit cell volume, allowing for more efficient storage of hydrogen. Fig. 1 shows the compression of unit cell volume as a function of pressure for the LiAlH_4 system. At 2.6 GPa, the structure transforms from monoclinic $P2_1/c$ to tetragonal $I4_1/a$ (NaAlH_4 type), and at 33.8 GPa to orthorhombic $Pnma$. We have carried out in-situ TOF neutron diffraction measurements using the high flux PEARL diffractometer at RAL, ISIS to investigate these theoretical predictions.

Fig. 2 shows the data series for LiAlH_4 loaded to 46 tons. Rietveld analysis reveals the start of a phase transition at ~ 4.2 GPa, that is characterised by the displacement in d-spacing of the reflections (130) and (01-3). The intensity of (130) is preserved, while (01-3) displays amorphisation. The observations indicate that planes in the cell that cannot be shifted will disorder, implying that the Li begins to disperse before the AlH_4 tetrahedra collapse. The data also show the presence of a new phase as broad reflections at ~ 2.1 and 2.2 Å. Model calculations of the LiAlH_4 structure in space group $I4_2/a$ show that this structure is not responsible for the extra reflections in the data.

The NaAlH_4 system does not display a phase transition to the highest pressure applied at 6.5 GPa.

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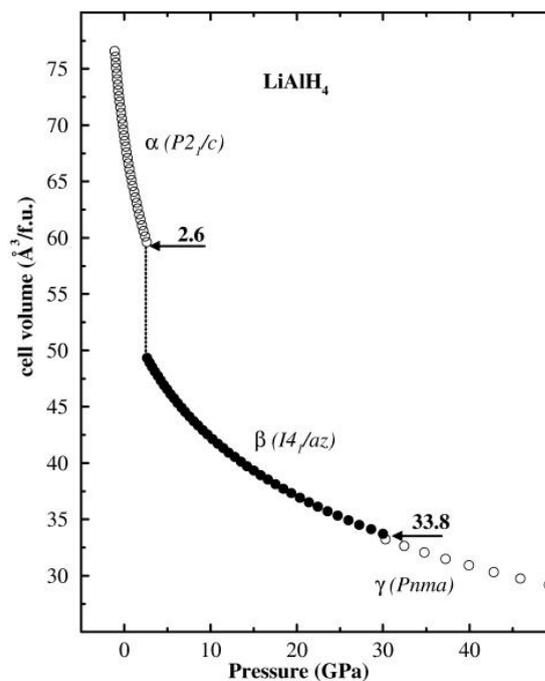


Fig. 1 The calculated equation of state for the LiAlH_4 system. The arrows indicate the transition pressures.

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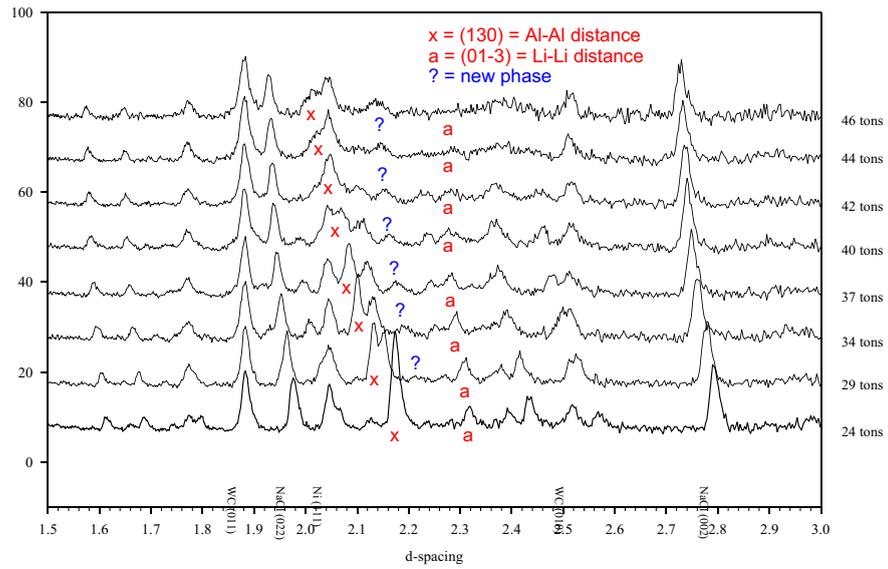


Fig. 2 Raw data series for the LiAlD₄ system from 20 tons load to 46 tons load.



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