

Neutron Diffractometer (SV28)



Instrument Parameters

	<i>Diffractometer 1</i>	<i>Diffractometer 2</i>
<i>Monochromator (reflection):</i>	Cu (220)	Cu (200)
<i>Wavelength:</i>	0.087 nm	0.124 nm
<i>Neutron flux density:</i>	2.5×10^6 n/cm ² s	2.55×10^6 n/cm ² s
<i>Mean FWHM of the Bragg reflections:</i>	0.5°	0.5°
<i>Detector, monitor:</i>	³ He tubes, fission chambers	
<i>Inner diameter of the Eulerian cradle:</i>	40 cm	25 cm
<i>Diffractometer control:</i>	PC 486 Linux, interface type Stoe, stepping motor drive (steps of 0.005°), angle encoders with a resolution of 0.005°.	

Instrument Responsible

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Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S28-04-013		
Experiment title:	Precursor effects at the paraelectric ferroelectric phase transition of RDP		
Dates of experiment:	06.06-28.06.2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
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Local Contact:	Anja Loose		

Experimental report text body

Potassium dihydrogen phosphate [KDP] is the most prominent member of an important group of hydrogen bonded ferroelectric crystals [1] of the composition $A(H,D)_2XO_4$ ($A=K, Rb, Cs, Tl, NH_4$; $X=P, As$). RDP, isomorphous to KDP and undergoes at 147(1) K a phase transition from the paraelectric phase with the tetragonal space group $I-42d$ ($F-4d2$) to the ferroelectric phase with the orthorhombic space group $Fdd2$. The localisation of the protons is specifically connected with the ferroelectricity. Most spectacular is the isotope effect, where upon replacement of H by D (deuteration), the transition temperature T_c increases from 123 K in KDP to 220 K in DKDP. To account for the isotope effect, Blinc has introduced the quantum-tunneling model of the protons in a double minimum potential. In [1] it was shown that already in the paraelectric phase the tetragonal structure is a superposition in time and space of the two possible ferroelectric orthorhombic structures (see figure 1). Therefore the double well potential is just a superposition of two adjacent in $[PO_4H_2]^-$ -groups in time and space.

To investigate the evolution of the structure at the ferroelectric paraelectric phase transition we have measured a set of integral Bragg reflections of a single crystal of RDP at the SV28. The quality of the crystal is of the same kind like the one used in [1] for the high resolution X-ray measurements and so far beyond the instrument resolution of the SV28. We have measured above 2500 reflections of which 301 are unique. The $R(int)$ of these reflections, averaged in the tetragonal space group is 5.4% and the $R(\sigma)$ 3.18%. In figure 2 the typical parameters of the standard reflections $(3\ 3\ 2)$, $(4\ 0\ 4)$ and $(4\ 4\ 0)$ are shown. A small change in the integral intensity is visible at longer times (higher index numbers) but no significant change in the FWHM/omega scan is visible.

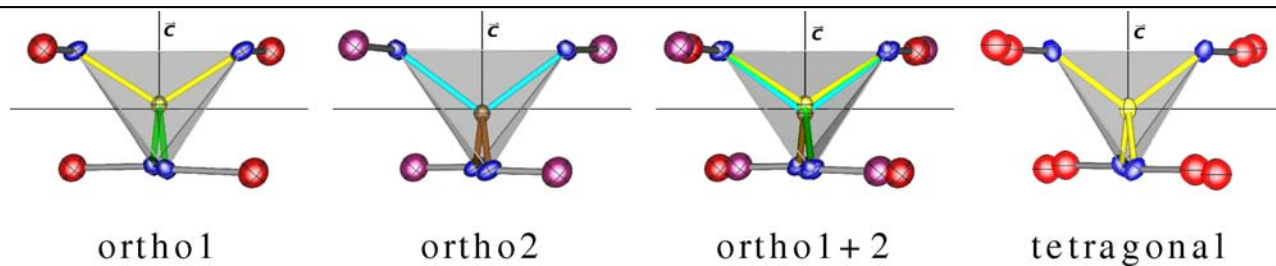


Illustration 1: $[\text{PO}_4\text{H}_2]^-$ -groups in RDP. Left to right: Ferroelectric orthorhombic phase, dipole down antiparallel c (state II); Ferroelectric orthorhombic phase, dipole up parallel c (state I); Superimposed state I and II; Paraelectric tetragonal phase

In the case of larger temperature fluctuations these values should change dramatically (splitting of reflections). Even the integral reflection should change dramatically due to a change in the extinction parameters (precursor effect [1]).

Now to make a long story short, we were not able to refine the structure successfully in the paraelectric phase. The refinement of the structure in the orthorhombic phase as well as a refinement of mixed structure is still in work.

[1] High resolution neutron and X-ray diffraction studies as a function of temperature and electrical field of the ferroelectric phase transition of RDP

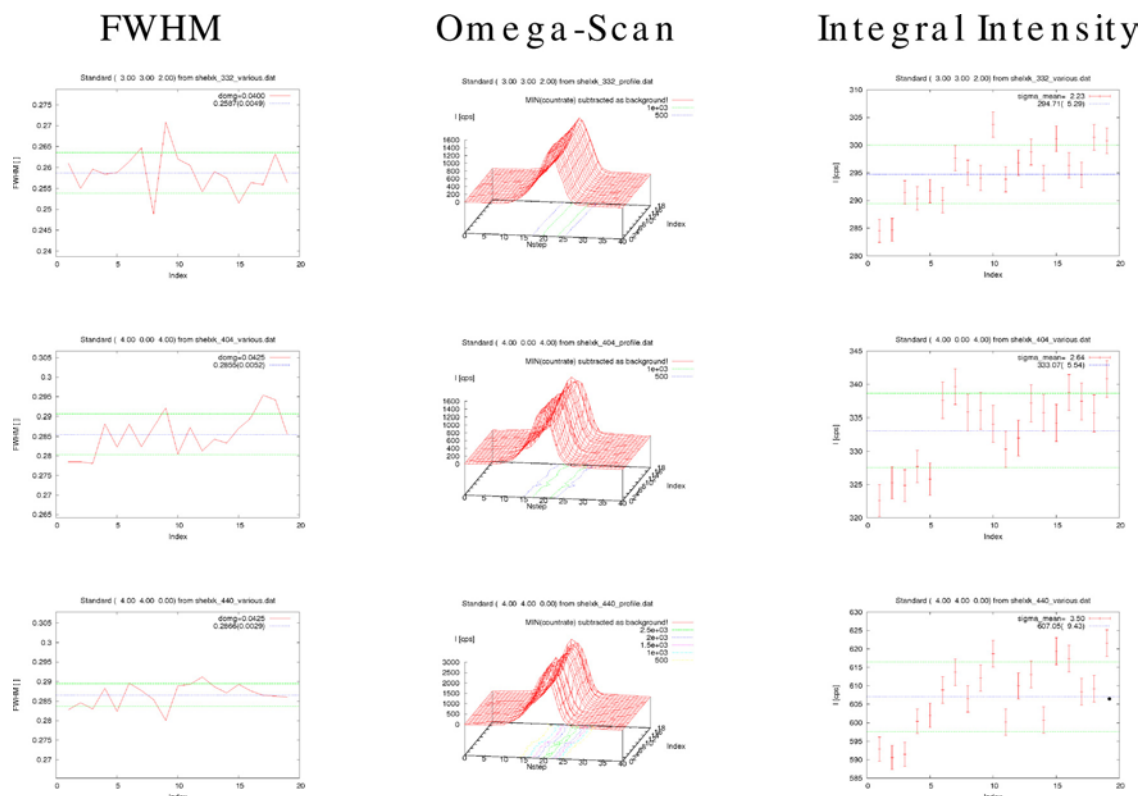


Illustration 2: FWHM, scan profile and integral intensity of standard reflections during the measurement of Bragg reflections 1.5K above T_c .



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S28-04-015		
Experiment title:	SrTiO ₃ – differences in the oxidised and reduced state		
Dates of experiment:	17.01.-30.01.2005 16.05.-22.05.2005	Date of report:	10.03.2006
Experimental team: Names	Addresses		
TIETZ, Frank	Forschungszentrum Jülich IWV-1		
Local Contact:	Dr. Anja Loose		

Experimental report text body

Strontium titanate (SrTiO₃) was selected as a model system for investigating the dimensional change after reduction and re-oxidation due to the valence changes of titanium. The interesting phenomenon in titanium-rich materials is the small shrinkage during reduction although an expansion is expected because of the increased cation radius like it is observed for lanthanum chromites ($\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$) or ceria materials ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$). In this study the compound SrTiO₃ was therefore investigated in more detail by single-crystal neutron diffraction (and XRD). The experiments should clarify a) any atomic displacement in the perovskite lattice and b) where the highest remaining electron density is located after subtracting the atoms from the structure refinement and c) if any additional interactions (bonds) can be deduced from the structure analysis.

For the measurement of the SrTiO₃ crystal in the oxidized state, a transparent colorless crystal with dimensions of about 2 x 4 x 0.5 mm was used. After the neutron scattering experiment the same crystal was exposed to a reducing atmosphere (Ar/4% H₂) at 1200°C to induce the reduction of Ti⁴⁺ to Ti³⁺ and the release of oxygen from the lattice compensating the reduction of the Ti ions. The crystal was heat treated for 100 h. Afterwards the sample had a deep black color and was used again for a second neutron scattering measurement.

The results of the neutron scattering experiments are summarized in Table 1.

Table 1: Results of the crystal structure determination before and after reduction

	SrTiO ₃ oxidised, RT,	SrTiO ₃ reduced, RT
Space group	Pm-3m	Pm-3m
Lattice parameter (Å)	3.922(5)	3.904(5)
Atomic position (x,y,z), Sr	0.500, 0.500, 0.500	0.500, 0.500, 0.500
Temp.factors (u ₁₁ , u ₂₂ , u ₃₃)	0.005(1), 0.005(1), 0.005(1),	0.003(2), 0.003(2), 0.003(2),
Atomic position (x,y,z), Ti	0.000, 0.000, 0.000	0.000, 0.000, 0.000
Temp.factors (u ₁₁ , u ₂₂ , u ₃₃)	0.0084(7), 0.0084(7), 0.0084(7)	0.0078(9), 0.0078(9), 0.0078(9)
Atomic positions (x,y,z), O	0.500, 0.000, 0.000	0.500, 0.000, 0.000
Temp.factors (u ₁₁ , u ₂₂ , u ₃₃)	0.002(1), 0.007(1), 0.007(1),	0.000(2), 0.005(2), 0.005(2),
wR ²	2,99 %	3,56 %
R ₁	1,74 %	1,77 %
Bond lengths (Å), Sr-O	2.773(4)	2.761(4)
Ti-O1	1.961(3)	1.952(3)
Ti-O2	3.397(4)	3.381(4)

The table clearly shows that no significant atomic displacement can be observed. By fixing the occupation factor of oxygen (full occupation) also no significant differences in the structure analysis appeared. This indicates that the amount of reduced Ti ions and released oxide ions are too small to be detected by neutron scattering. The only small but significant change of the crystal structure is the decrease of the lattice parameter by about 0.5 % and hence resulting in a small decrease of the bond lengths.

This result agrees very well with a dilatometry experiment in which a similar crystal was reduced and re-oxidised *in-situ* giving a length change of 0.3 % at 1000°C. The subsequent investigations performed on single crystals (electrical conductivity, thermogravimetry, dilatometry) have shown that the changes of the properties during redox cycling are much smaller for a single crystal than for polycrystalline ceramics. Therefore the results of the neutron experiments fit very well with the other observations. However, the major aim of these investigations, i. e. the explanation of the shrinkage after reduction of the material, could not be obtained.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S28-05-002		
Experiment title:	Structural behaviour of topaz at low temperature		
Dates of experiment:	04.04.-24.04.05 and 09.05.-22.05.05	Date of report:	06.02.06
Experimental team: Names	Addresses		
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Local Contact:	Dr. Anja Loose		

Experimental report text body

The crystal structure of a natural topaz (ideal formula $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$) was reinvestigated by means of single-crystal X-ray diffraction (at 298K) and neutron diffraction (at 298 and 10K) and polarized infrared spectroscopy in order to define unambiguously the real symmetry of topaz, the location of the proton and its thermal displacement parameters at room and low-temperature, the hydrogen-bonding and the vibration modes (stretching and bending) of the OH dipole. A single-crystal of natural topaz $[\text{Al}_{2.00}\text{Si}_{1.05}\text{O}_{4.00}(\text{OH}_{0.26}\text{F}_{1.75})]$, $2 \times 3 \times 13 \text{ mm}^3$ from Ouro Preto, Minas Geras, Brasil was used for the neutron diffraction experiments at 298 and 10K with a Huber four-circle diffractometer (SV28/1) installed at the DIDO reactor – FZJ. A He-cryostat was used for the low- T experiment. The incident radiation (obtained using a Cu(200) single-crystal monochromator) with a constant wavelength of $0.87238(1)\text{\AA}$ was used for the room and low- T experiments. The neutron flux density was about $2.5 \cdot 10^6 \text{ n} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$ and the tangential beam tube gave rise to a very small background count rate ($\sim 5 \text{ s}^{-1}$). A total of 4446 reflections (of which 988 unique) were recorded at 298K (maximum $2\theta = 99.93^\circ$) and 4049 reflections (of which 632 unique) at 10K (maximum $2\theta = 82.26^\circ$). The systematic extinction rules in general agreed with the space group $Pbnm$. However, we observed 6 and 14 violating reflections for the data collections at 298 and 19 K respectively, belonging to the classes $00l$ (with $l=2n+1$), $0kl$ (with $k=2n+1$) and $h0l$.

Intensity of the diffraction data was corrected for Lorentz effect and no absorption correction was applied because of the composition and the dimensions of the sample. The discrepancy factors for the symmetry related reflections were $R_{int} = 0.0229$ and $R_{int} = 0.0251$ at 298 and 10 K respectively. The neutron diffraction data were first processed with the program E-STATISTICS, implemented in the WinGX package (Farrugia 1999). The structure of topaz was found to be centrosymmetric at 92.6%. Then, the diffraction data were processed with the program ASSIGN-SPACEGROUP (in WinGX, Farrugia 1999). Two possible space groups (both belonging to the mmm Laue class) were selected by the program: $Pbmn$ and $Pbn2_1$. However, the Combined Figure of Merit (CFOM) showed unambiguously that the space group $Pbnm$ is highly likely (CFOM $-Pbnm = 0.729$, CFOM- $Pbn2_1 = 9.178$). The crystal structure refinement was then performed in the space group $Pbnm$ using the SHELX-97 software (Sheldrick 1997) with anisotropic thermal displacement parameters and starting from the atomic coordinates of Alberico et al. (2003).

X-ray and neutron structural refinements allow us to infer that the crystal structure of natural topaz with $OH/(OH+F) < 0.5$ can be described with the $Pbnm$ space group. Violating reflections, found in the previous investigations and in this study, are likely due to Renninger effect (double diffraction phenomenon). The nuclear density Fourier map shows that the proton is located at Wyckoff $8d$ position and the refined coordinates are: $x=0.495(2)$, $y=0.252(1)$, $z=0.1629(7)$ (Fig. 1). The O-H bond lies on the (010)-plane and forms an angle of about 28.9° with the c -axis. Neutron structural refinements at 298 and 10K show that the displacement ellipsoid of the proton is highly anisotropic. The H-bonding arrangement appears to be much more complex than that reported in previous studies, with at least four potential $H\cdots O$ or $H\cdots F$ interactions (distances $< 2.38\text{\AA}$).

References

- Alberico, A., Ferrando, S., Ivaldi, G., and Ferraris, G. (2003) European Journal of Mineralogy, 15, 875-881.
 Farrugia, L.J. (1999) Journal of Applied Crystallography, 32, 837-838.
 Sheldrick, G.M. (1997) SHELX-97. Programs for crystal structure determination and refinement. Institute of Inorganic Chemistry, University of Göttingen, Germany.

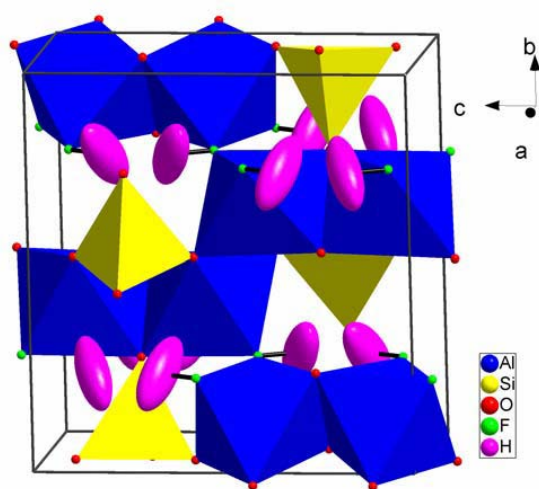


Fig. 1. Clinographic view of the crystal structure of topaz



Experimental Report
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Proposal number:	S28-05-003		
Experiment title:	Structure refinement and location of protons in natural cancrinite Na₈[Si₆Al₆O₂₄]*CO₃*2H₂O		
Dates of experiment:	23.05.-29.05.2005 06.06.-15.06.2005	Date of report:	09.03.2006
Experimental team: Names	Addresses		
Dr. G. Redhammer	FB Materialwissenschaften, Abteilung Mineralogie, Universität Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, Österreich.		
Prof. Dr. G. Roth	Institut für Kristallographie, RWTH Aachen, Jägerstr. 17/19, D-52056 Aachen, Deutschland		
Prof. Dr. G. Della Ventura	Dipartimento di Scienze Geologiche, Università di Roma Tre, Largo S. Leonardo Murialdo 1, I-00146 Roma, Italy		
Local Contact:	Dr. Anja Loose (IFF)		

Experimental report text body

Cancrinite belongs to the group of feldspathoids, which are framework aluminosilicates comprising at least three distinct groups: the leucite, nepheline-kalsilite and cancrinite-sodalite groups. The cancrinite-sodalite group in particular, comprises all phases characterized by three-dimensional connection of six-member rings of silicon and aluminium tetrahedra; each ring is linked to three rings in a preceding layer and to three rings in the succeeding one, such as to form a three dimensional framework. In cancrinite the stacking sequence of these tetrahedral rings gives rise to channels and cavities filled by extra-framework anions and cations. Typical anions within the structural channels are H₂O, OH, and CO₃²⁻. Also Na⁺ and Ca²⁺ are located within these channels and pores. To try to locate hydrogen within the channel, two natural cancrinite samples, one from Kameron, #29509, and one from Kanada, Bancroft #38834 were analysed. Preliminary X-ray diffraction experiments showed both samples to be commensurate, while a second sample of Kanada (# 38855) revealed incommensurate superstructure reflections.

Both cancrinite samples are trigonal, space group *P*6₃, lattice parameters are *a* = 12.595(5) Å, *c* = 5.121(5) Å (#29509) and *a* = 12.60(2) Å, *c* = 5.121(5) Å (#38834) respectively. Data sets for both samples were refined *R* = 2.18 % and 4.17 % respectively. The samples show perfectly ordered Al, Si distribution with average Si-O and average Al-O bond lengths of 1.613(3) Å and 1.732(3) Å. Two positions for the alkali cations are present in the structure, one is located within the cancrinite cage (Na1), and the other one is within the large channel. It was found that the cage position is occupied by sodium only, while both Na and Ca are hosted at the channel site. The (Na,Ca) cations are bonded to three oxygen atoms of the Al-Si framework at a distance of ~ 2.40 Å and to oxygen atoms of a CO₃ groups. The two non-equivalent CO₃ groups show large anisotropic displacements in channel direction and have occupancy of ~ 1/3. Because of the close proximity of the positions, only one can be occupied at any one time.

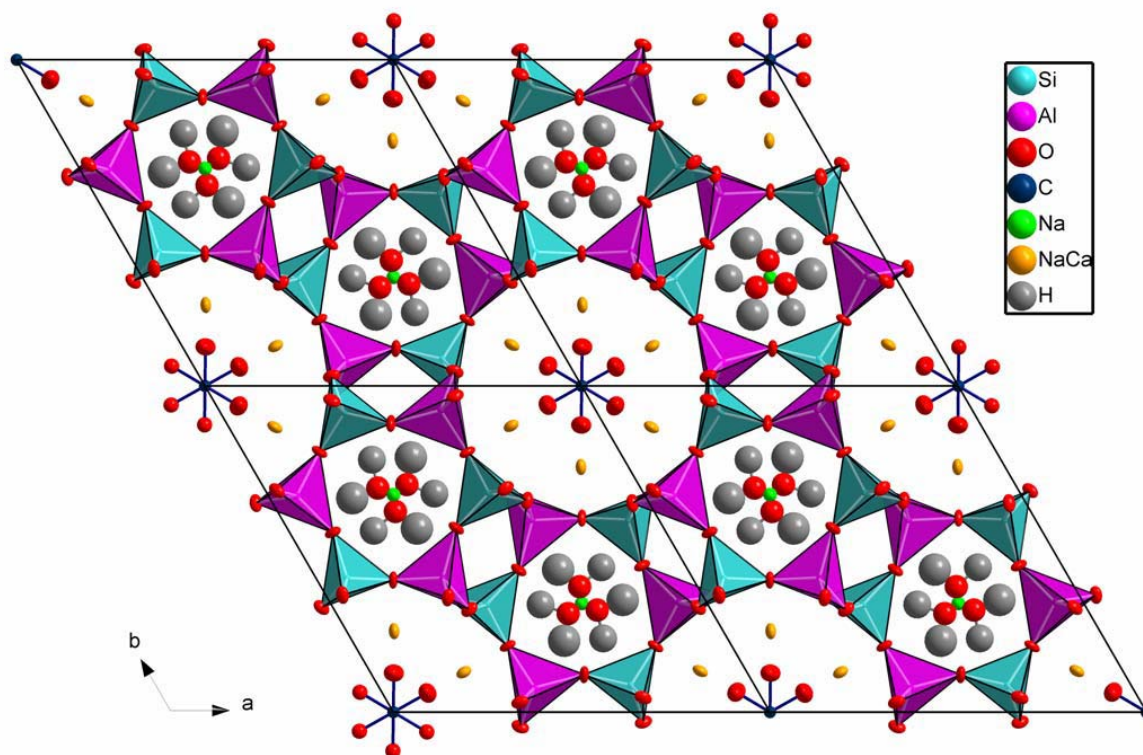
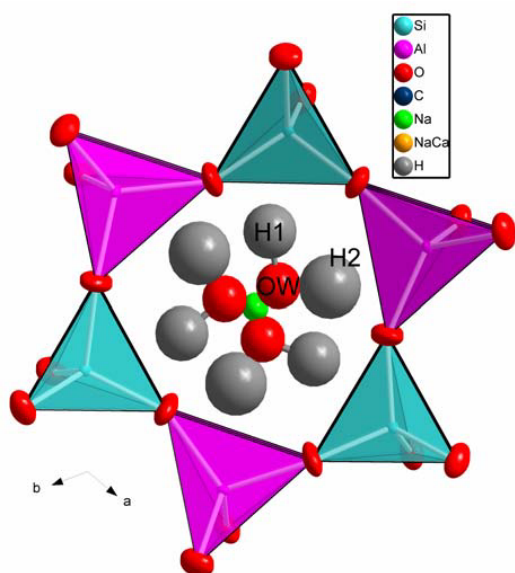


Figure 1: View of the cancrinite structure along the c - axis, showing CO_3 groups and NaCa sites within the large channels and Na-sites and H_2O molecules within the cancrinite cage.

Detailed inspection of the CO_3 groups show that they are not perfectly coplanar with C-O bond lengths of 1.308(3) Å and 1.293(3) Å for the C1 and the C2 site respectively.



The cancrinite cage hosts sodium at the Na1 site. Thereby sodium is planar coordinated by 6 oxygen atoms of the Al-Si framework at distances of 2.436(3) Å and 2.859(3) Å. Additionally there are two bonds to the oxygen atom of the water molecule at distances of 2.379(7) and 2.874(7) Å. This oxygen atom is located at a general position near the triad axis. Due to short O-O distances of 0.98(1) Å only one of the three possible positions can be occupied at one time and the maximum occupation of this general site is 0.33. This is actually the case as shown by refinements of the X-ray diffraction data, while the neutron data show a somewhat higher occupation of 0.42. Inspection of difference electron density maps revealed some residuals close to this oxygen atom at distances of ~ 1 Å. Putting hydrogen atoms to these residuals and allowing to refine the occupation of these sites gave reliable O-H distances of 0.95(2) Å and 0.98(2) Å with an occupancy close to 0.4; the H1-Ow-H2 angle amounts 99.3(9)°. The isotropic atomic displacement of the hydrogen atoms is quite large, and in detailed inspection it may be

followed that there is a splitting of the H1 and H2 positions and there are a total of four quite well defined hydrogen positions around Ow. The occupancies are between 0.12 and 0.18, the isotropic atomic displacement parameters are similar for all for H with $U \sim 0.05 - 0.06$.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S28-05-003/2		
Experiment title:	Structure refinement on natural Hauyne, ideally $\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2$		
Dates of experiment:	15.06.-28.06.2005	Date of report:	30.03.2006
Experimental team: Names	Addresses		
Dr. G. Redhammer	FB Materialwissenschaften, Abteilung Mineralogie, Universität Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, Österreich.		
Prof. Dr. G. Roth	Institut für Kristallographie, RWTH Aachen, Jägerstr. 17/19, D-52056 Aachen, Deutschland		
Prof. Dr. G. Della Ventura	Dipartimento di Scienze Geologiche, Università di Roma Tre, Largo S. Leonardo Murialdo 1, I-00146 Roma, Italy		
Local Contact:	Dr. Anja Loose (IFF)		

Experimental report text body

1. Introduction

Hauyne, ideally $\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2$ is a sulphatic sodalite - group mineral. The structure has 4-membered rings of AlO_4 and SiO_4 tetrahedra that are parallel to the $\{1\ 0\ 0\}$ direction. These rings are connected to form a 3-dimensional framework with 6-membered rings parallel to the $\{1\ 1\ 1\}$ direction giving rise to to cube-octahedral cages. According to literature, the alumino-silicate framework of hauyne has a 1 : 1 Al : Si ratio and these atoms are fully ordered (Hassan & Grundy 1991). The cages can accommodate a large variety of cations such as K^+ , Na^+ and Ca^{2+} , with SO_4^{2-} groups as the dominant interstitial anions. Members of this mineral group may also show complex satellite reflections. However, the sample of blue hauyne from Alban Hills, Italy, we have studied, does not show any satellite reflections as proven by preliminary X-ray diffraction experiments. Polarized infra-red experiments hint the presence of a small amount of OH^- within the cages.

2. Results and Discussion

The sample of blue hauyne is cubic, space group $P-43n$, $a = 9.116(5)\text{ \AA}$, $Z = 1$. Structure solution using direct methods revealed the positions of Al, Si and oxygen, building up the alumino-silicate framework. Interstitial cations and anions were located from difference density maps. The final refinement using full anisotropic atomic displacement parameters for the framework atoms converged to final agreement factors $R_1 = 2.28\%$ and $wR_2 = 6.43\%$ for all 186 unique reflections. During refinements a mixed occupation of Al and Si position was tested, however, Al and Si indeed appeared to be fully ordered on the two tetrahedral coordinated framework sites. Figure 1 displays the topology of the structure view in 2 different directions.

Within the channels in $\{1\ 1\ 1\}$, possible positions for cations Na^+ , K^+ and Ca^{2+} were easily located $x = 0.681(2)$, $0.719(2)$ and $0.754(2)$ respectively. These positions are only partly filled, giving rise to occupancy of 0.46 for K, 0.28 for Ca and 0.263 for Na respectively. These values correspond well to the chemical composition of the compound as determined from electron microprobe analysis.

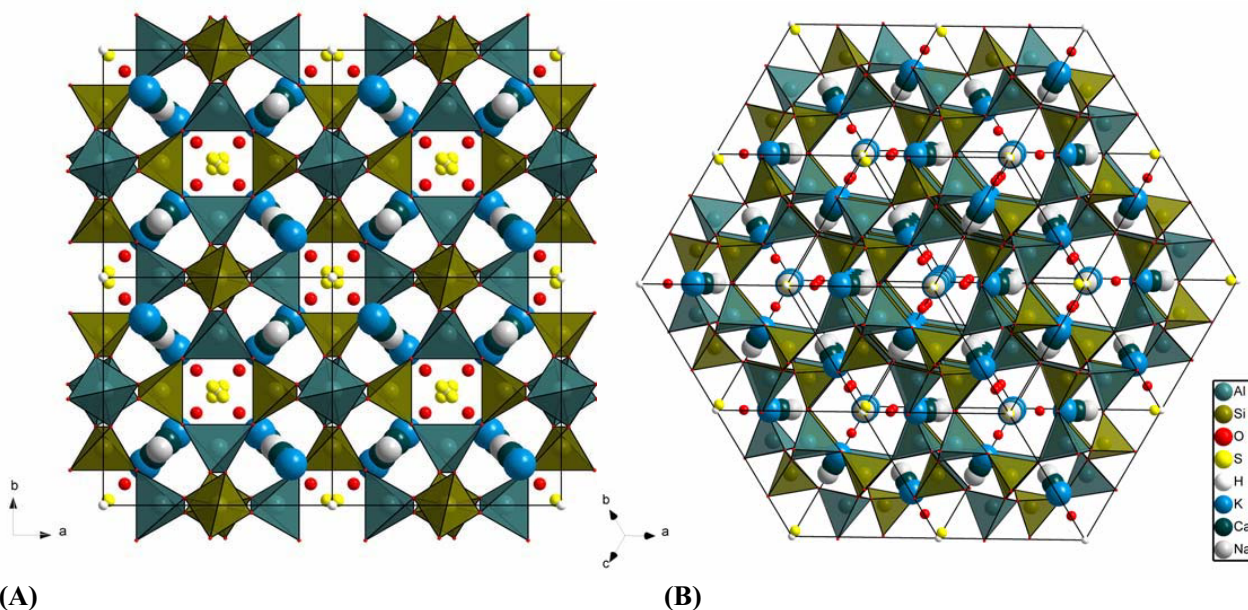


Figure 1: Structure of blue Hauyne, **(A)** viewed along the crystallographic a -axis and displaying the four-member rings of edge-sharing AlO_4 and SiO_4 tetrahedra. **(B)** viewed almost along the $\{1\ 1\ 1\}$ direction showing the channels formed by the arrangement of aluminosilicate framework. Cations Na^+ , K^+ and Ca^{2+} alternate with SO_4 groups within the channels.

Interpretation of differenced densities arising from SO_4 groups appeared to be difficult. The sulfur atom is displaced from $2(a)$ position at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ to a $8(e)$ position with (x, x, x) , $x = 0.479(2)$, the occupancy was fixed to 0.25 as due to the closeness of S-atoms due to fourfold axis the site can only be occupied by $\frac{1}{4}$. Oxygen atoms (O_2) coordinating the S-atom(s) were found at (x, x, x) $x = 0.594(2)$ giving rise to three reasonable S-O bond lengths of $1.45(4)$ Å, while one is $1.70(4)$ Å. However, isotropic displacements especially for the oxygen are very large and some residual density appears in Fourier maps which might be interpreted as oxygen atoms. One of these peaks could be interpreted as oxygen atom (O_3) belonging to the SO_4 group with S-O bond length of $1.38(2)$ Å. A negative difference peak at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ may be interpreted as an H atom with an oxygen atom (O_4) being away $1.07(6)$ Å with almost the same occupancy of $\sim 1/3$.

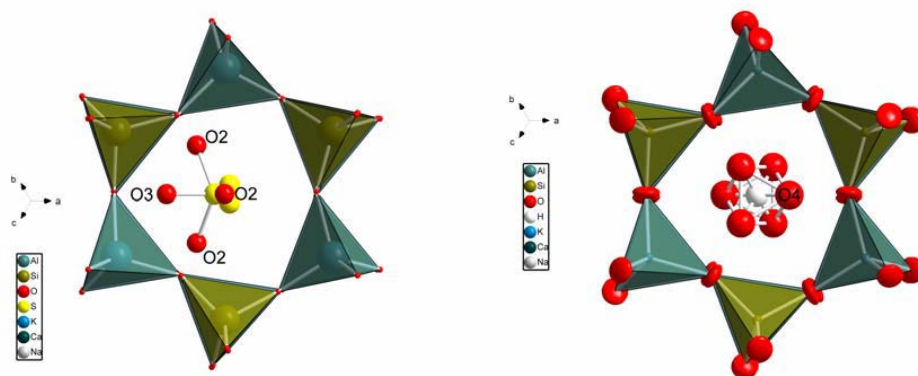


Figure 2: Possible arrangement of SO_4 and OH^- groups in hauyne $\{1\ 1\ 1\}$ channels.

References cited:

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Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S28-05-007		
Experiment title:	High-temperature structural behavior of epidote, $\text{Ca}_2(\text{Al, Fe})_3(\text{SiO}_4)_3(\text{OH})$		
Dates of experiment:	24.10.-13.11. and 28.11.-18.12.2005	Date of report:	06.02.06
Experimental team: Names	Addresses		
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Local Contact:	Dr. Anja Loose		

Experimental report text body

Epidote group of minerals are monoclinic sorosilicates (with mixed SiO_4 tetrahedra and Si_2O_7 groups) with general formula $\text{A}_1\text{A}_2\text{M}_1\text{M}_2\text{M}_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, M represent trivalent cations in octahedral sites and A represent divalent cations in larger coordination (Fig. 1). The crystal structure of epidote is built up by two types of endless octahedral chains, parallel to $[010]$, consisting of three non equivalent M1, M2 and M3 octahedra. The proton is bonded to the oxygen site O10 of the M2 polyhedron, with a hydrogen bridge to the O4 site of the neighboring M1 octahedron (following the site notation of Kvik et al. 1988) (Fig. 1). The monoclinic epidote minerals have space group $P2_1/m$. However, on the basis of some spectroscopic investigations, a possible reduction of the symmetry to Pm or $P-1$ space group due to “Al/Fe convergent ordering” on M3 was suggested (Franz & Liebscher 2004). Despite the crucial role of natural epidotes in high-pressure/high-temperature metamorphism, no structural investigation of epidotes under non-ambient conditions has been performed. Therefore, the high- T structural evolution of a natural epidote $[\text{Ca}_2(\text{Al, Fe})_3(\text{SiO}_4)_3(\text{OH})]$ from the intrusive/metamorphic complex of Val Sissone, (Rhetic Alps, Italy) was investigated by means of single-crystal neutron diffraction at 23 and 700°C in order to define unambiguously the real symmetry of epidote at high- T , the location of the proton and its thermal displacement parameters at room and high- T , the hydrogen-bonding evolution with T and/or any potential dehydration (deoxydrilation) effect. The diffraction experiments at room and high- T were performed with a Huber four-circle diffractometer (SV28/1) installed at the DIDO reactor – FZJ. A furnace designed at the FZJ was used for the high- T experiment. The incident radiation (obtained using a Cu(200) single-crystal monochromator) with a constant wavelength of $0.87238(1)\text{\AA}$ was used for the room and high- T experiments.

A total of 2228 unique reflections were recorded at 23°C ($2\theta_{max} = 95.04^\circ$) and 1721 reflections at 700°C ($2\theta_{max} = 82.24^\circ$). The systematic extinction rules agreed with the space group $P2_1/m$. The structural refinement with the diffraction data collected at room and high- T was performed in space group $P2_1/m$ at first with isotropic displacement parameters using the SHELXL-97 package (Sheldrick 1997), starting with the atomic coordinates of Kvik et al. (1988). The final least-square cycles were conducted with anisotropic thermal parameters and all the principal mean square atomic displacement parameters were positively defined. The Al/Fe fraction at the M1, M2 and M3 octahedral sites was refined. At the end of the refinements, no peak larger than $\pm 0.68 \text{ fm}/\text{\AA}^3$ and $\pm 1.20 \text{ fm}/\text{\AA}^3$ were found in the difference-Fourier map of the nuclear density at 23 and 700°C respectively. The final agreement indexes (R_1) were $R_1(23^\circ\text{C})=0.0309$ and $R_1(700^\circ\text{C})=0.0562$ for 127 refined parameters. Neutron structural refinements allowed us to infer that the crystal structure of natural epidote is stable at least up to 700°C and no deoxydrilation effect occurs. We can also infer that at room- T the octahedral M1 site shows a low amount of iron [%Fe=2.2(4)%], which is absent at the M2 site. In contrast, a high content of Fe is observed at the M3 site [%Fe=71.6(5)%]. At 700°C, we do not observe any statistically relevant difference of the cations distribution in the octahedral sites with respect to that observed at room- T [%Fe_{M1}=0.6(12)% and %Fe_{M3}=70.4(14)%]. At present, we have no evidence of any T -induced order-disorder phenomena concerning the Al/Fe distribution in the M1-M2-M3 octahedral sites (the so called “non-convergent ordering”) or any high- T phase transition to lower symmetry due to Al/Fe “convergent ordering” on M3 (with a splitting of M3 into two sites: M3 and M3’, Franz & Liebscher 2004).

References

- Kvik Å, Pluth JJ, Richardson Jr JW, Smith JV (1988) Acta Cryst B, 44, 351-355.
 Franz G, Liebscher A (2004) Rev. Min. Geoch., 56, 1-80.
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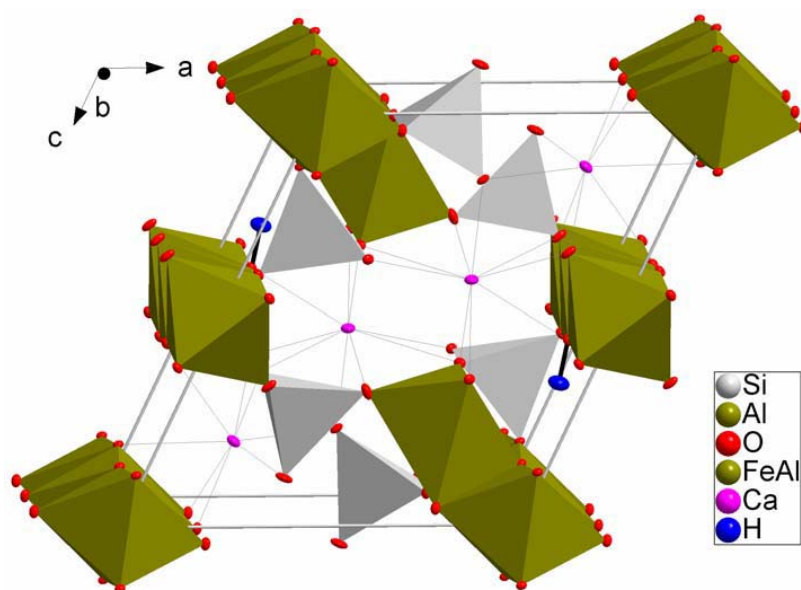


Fig. 1. Clinographic view of the crystal structure of epidote



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S28-05-008		
Experiment title:	Crystal structure analysis of (1-x)PZN-xNBT		
Dates of experiment:	10.12.-18.12.2005 09.01.-22.01.2006	Date of report:	05.06.2006
Experimental team: Names	Addresses		
Dr. Loose, Anja	IFF,FZ-Jülich and Institut für Kristallographie, RWTH Aachen Jägerstr.17-19, D-52056 Aachen		
Prof. Dr. Heger, Gernot			
Dr. Park, Hyun Min	Korea Research Institute of Standards and Science (KRISS) Materials Evaluation Center, P.O.Box 102, Yusong, 305-600, Korea		
Local Contact:	Dr. Loose, Anja		

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The new ferroelectric material $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$, abbreviated as PZN-NBT, has been developed for piezoelectric application. Large single crystals of PZN-NBT up to several cm diameter were grown by the flux method at about 700°C in the cubic Perovskite-structure.

In order to investigate the phase diagram of PZN-NBT as function of temperature and NBT content x , neutron diffraction measurements were performed at the single crystal diffractometer SV28(left) for compositions $x = 0.05, 0.10$, and 0.15 .

Rietveld profile refinements on synchrotron X-ray powder patterns obtained at room temperature with samples of the same nominal compositions yield the polar space group $P4mm$. According to the symmetry relation between the cubic high-temperature phase of space group $Pm\bar{3}m$ and the tetragonal modification of space group $P4mm$, there exists 3 twin states with 6 differently oriented ferroelectric domains which may occur at room temperature.

The Bragg-reflections of the multi-twinned crystals are split leading to a broad mountain-like ω -scan profile of typically 1.6° FWHM for a sample of $x = 0.15$. On heating the reflection splitting is lowered more or less linearly with increased temperature up to about 400 K, where there occurs a jump-like reduction to $\text{FWHM} = 0.27^\circ$ which corresponds to the instrumental resolution for high quality single crystals (Fig.2). The discontinuous behaviour of the tetragonal to cubic phase transition (of 1st order) is even more pronounced in case of the intensity data (Fig. 3). The integrated intensity of the sum of the domains remains almost constant up to about 400 K. The small intensity reduction in this range may be attributed to a normal increase of temperature Factors (Debye-Waller). The giant fall from 3700 to 1400 is a signature of the disappearance of the ferroelectric domains: the crystal recovers and according to its good quality extinction effects lead to an important reduction of Bragg-intensities in the cubic high temperature phase. Both observations (integrated intensity and FWHM) are completely reversible on cooling with a hysteresis of about 5.8 K.

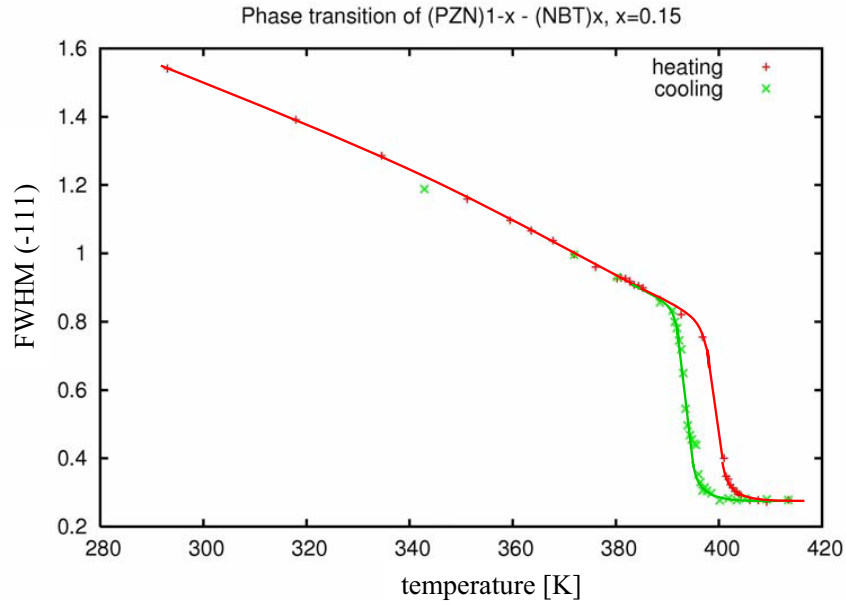


Fig. 1

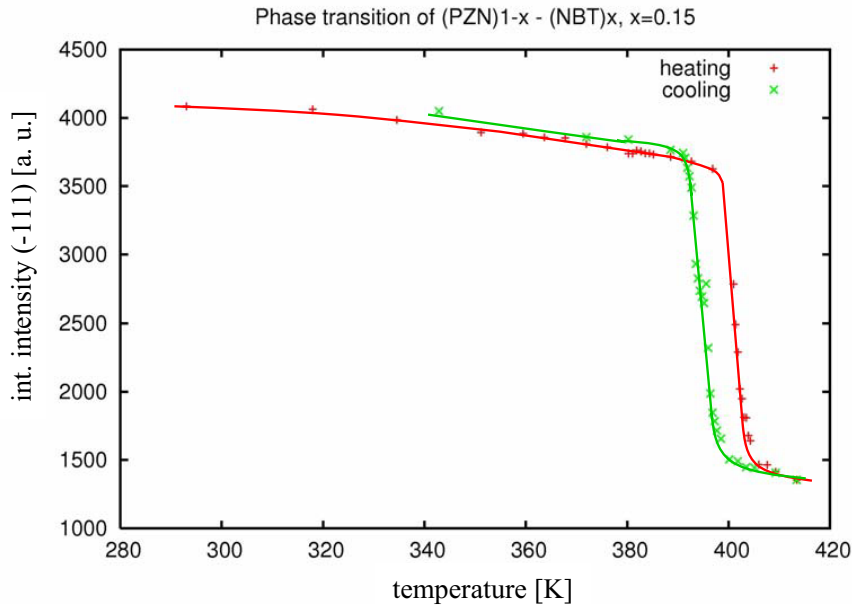


Fig. 2

For the structure refinement of the crystal with composition $x = 0.15$, based on a complete data set obtained at 420 K, the effective neutron scattering lengths for the A- and B- sites of the ABO_3 Perovskite-structure were calculated according to the nominal composition. The resulting R-factor of 2.6% is very good. It seems that the oxygen sublattice is fully occupied whereas there might be indication for either some vacancies on the B-site or a smaller modification of composition.

For the $x = 0.10$ crystal the ferroelectric phase transition occurs at about 394 K on heating. A complete data set of Bragg-intensities was measured at 413 K. The results of the structure refinement correspond to those of $x = 0.15$. The $x = 0.05$ crystal showed at room temperature no splitting of reflections or even significant increased widths (FWHM). Therefore, a complete set of intensity data was measured at room temperature and also refined in the cubic Perovskite structure type. For all compositions there is an important difference between the mean-square displacements of sites A and B. The octahedron-coordinated B-sites show small U_{ij} values, whereas those of the cubeoctahedron-coordinated A-sites are very large. It seems that the localisation of $Pb^{2+}/Na^{1+}/Bi^{3+}$ with its different ionic radii may give rise to static contributions in the O_{12} -cubeoctahedron.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S28-05-009		
Experiment title:	Crystal structure and proton ordering of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$		
Dates of experiment:	23.01.06-27.01.06 06.02.06-18.02.06 26.04.06-28.04.06	Date of report:	02.06.06
Experimental team: Names	Addresses		
Prof. Dr. Heger, Gernot	Institut für Kristallographie, RWTH Aachen Jägerstr. 17-19, D-52056 Aachen		
Sohn, Yoo Jung			
Dr. Loose, Anja			
Local Contact:	Dr. Loose, Anja		

Experimental report text body

$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (TAHS) is a representative of the ferroelastic $\text{M}_3(\text{H/D})(\text{AO}_4)_2$ -structure family with monovalent M^+ -ions ($\text{M}^+=\text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+/\text{ND}_4^+$) and $\text{A}=\text{S}, \text{Se}$ which is characterized by strong hydrogen bonds between the AO_4 -groups forming $\text{AO}_4\text{-H/D-AO}_4$ -dimers. The $\text{M}_3(\text{H/D})(\text{AO}_4)_2$ -compounds show a rich variety of polymorphic phases where the phase transitions are related to ordering phenomena of the $\text{AO}_4/\text{N}(\text{H/D})_4$ -groups and the H/D -atoms in the O-(H/D)-O hydrogen bonds. Neutron diffraction studies on single crystals are needed to determine the hydrogen distributions in the crystal structures of the TAHS-phases in detail. This information is essential for to clarify the mechanisms of phase transitions driven by H-ordering.

Large perfect single crystals of TAHS were grown from aqueous solution in the room temperature phase II. A sample of $3 \times 3 \times 3 \text{ mm}^3$ was used for the measurement of a complete set of reflection intensities at the SV281-diffractometer ($\lambda=0,87238 \text{ \AA}$) up to $(\sin\theta/\lambda)_{\text{max}}=0,7 \text{ \AA}^{-1}$ at room temperature. In order to reduce extinction effects the sample crystal was quenched in liquid nitrogen. A careful analysis of systematic extinctions confirmed that $h0l$ reflections with $l=2n+1$ are absent in accordance with the monoclinic space group $\text{C } 12/c1$, proposed by X-ray diffraction studies [1, 2]. An additional investigation by ψ -scan technique on $h0l$ reflections with $l=2n+1$ using a much larger crystal ($6 \times 7 \times 8 \text{ mm}^3$) confirmed this result. Even with much increased statistics there was no indication of these “forbidden” reflections. The results of the crystal structure refinement on neutron diffraction data of TAHS II are in agreement with those of the X-ray analyses [1, 2]. The additional new findings consist in

- the dynamical hydrogen-disorder with a double-minimum-potential in the $\text{O1-H1}\cdots\text{H1-O1}$ bridge of the $(\text{SO}_4\text{-H-SO}_4)$ dimers. This is clearly visible from the anisotropic mean square displacements of H1 in Fig. 1.
 - the pronounced librations of the $(\text{NH}_4)^+$ -cations around their well defined N1/N2 positions (see Fig. 2.). This can be interpreted as a consequence of competing $\text{N-H}\cdots\text{O}$ hydrogen bonds leading to a dynamical disorder.
- A structure refinement including rigid body rotations of the NH_4 groups is in preparation.

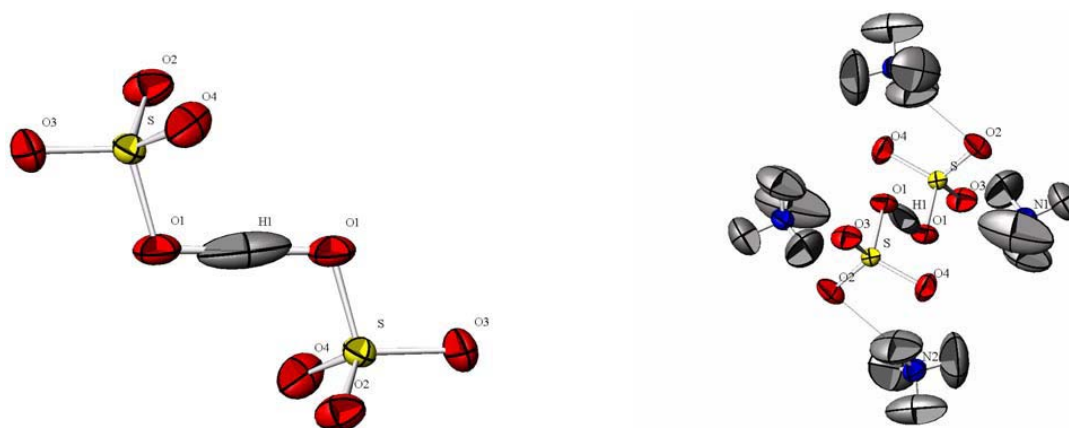


Fig. 1. Two SO_4 -tetrahedra connected by an H-bond Fig. 2. $\text{SO}_4\text{-H1-SO}_4$ dimer with surrounding NH_4 -groups forming a dimer.

The phase transition between the room temperature phase II and the high temperature phase I was studied by measurements of the integrated intensity of a reflection which does not exist in the high temperature phase I (space group $R\bar{3}m$ or $R\bar{3}$). Fig. 3. shows the temperature dependent intensity of the $-2\ 2\ 1$ -reflection. The phase transition temperature determined at $140\pm 2^\circ\text{C}$ corresponds very well to the literature data (140°C).

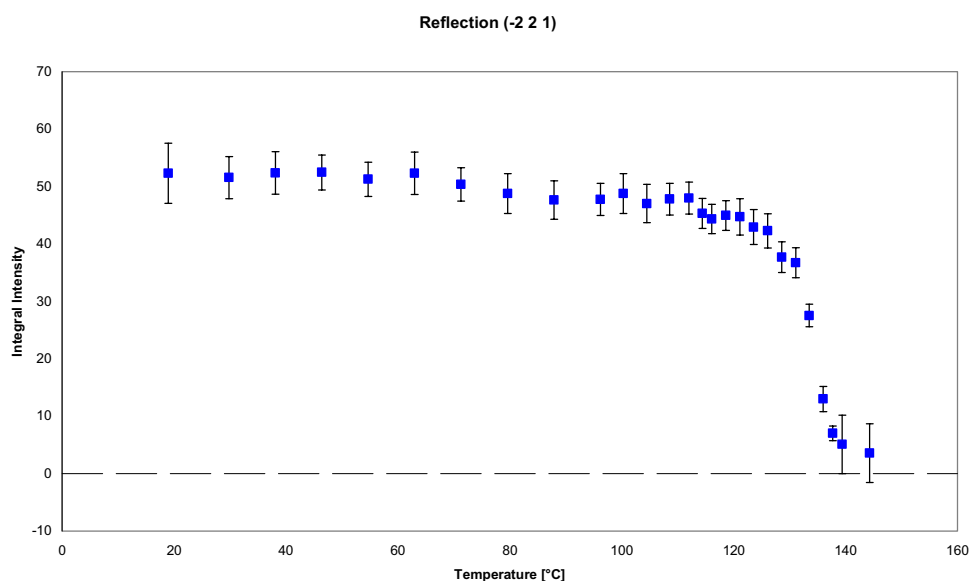


Fig. 3. Temperature dependency of integral intensity of the $-2\ 2\ 1$ -reflection.

The reflection profiles at high temperature for $T > T_c$ (II-I) are considerably enlarged. Therefore, it was impossible to obtain reliable integrated reflection intensities in the high temperature phase I of TAHS up to now. We plan to repeat this experiment at high temperature with an unquenched crystal, where we expect better defined reflection profiles.

Temperature dependent X-ray powder diffraction measurements on the II-I phase transition of TAHS confirm the neutron results very well.

- [1] K.Friese, M.I.Aroyo, L.Schwalowsky, G.Adiwidjaja, U.Bismayer, Solid State Chem. **165**, 136 (2002)
- [2] P.M. Dominiak, J.Herold, W.Kolodziejski, K.Wozniak, Inorg.Chem. **42**, 1590 (2003)

Institut für Festkörperforschung Forschungszentrum Jülich GmbH D-52425 Jülich			
Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor			
Proposal number:	S28-05-007/2		
Experiment title:	High-temperature structural behavior of epidote, $\text{Ca}_2(\text{Al, Fe})_3(\text{SiO}_4)_3(\text{OH})$ (Second Experiment)		
Dates of experiment:	07.-20. April 2006	Date of report:	10.05.2006
Experimental team:			
Names	Addresses		
G. Diego Gatta	Dipartimento di Scienze della Terra, Università degli Studi di Milano, I-20133 Milano, Italy		
Local Contact:	Dr. Anja Loose		

Experimental report text body

Epidotes are monoclinic sorosilicates (with mixed SiO_4 tetrahedra and Si_2O_7 groups) with general formula $\text{A}_1\text{A}_2\text{M}_1\text{M}_2\text{M}_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, M represent trivalent cations in octahedral sites and A represent divalent cations in larger coordination (Fig. 1). The crystal structure of epidote is built up by two types of endless octahedral chains, parallel to $[010]$, consisting of three non equivalent M1, M2 and M3 octahedra. The proton is bonded to the oxygen site O10 of the M2 polyhedron, with a hydrogen bridge to the O4 site of the neighboring M1 octahedron (following the site notation of Kvik et al. 1988) (Fig. 1). The monoclinic epidote minerals have space group $P2_1/m$.

In the first experiment performed by us at the FZJ on the high- T structural behaviour of epidote, $\text{Ca}_2(\text{Al, Fe})_3(\text{SiO}_4)_3(\text{OH})$, we investigated the T -induced structural evolution of this sorosilicate and the main deformation mechanism on the basis of two data collection and structural refinements at room conditions and at 700°C , respectively. However, the high- T data at 700°C were not suitable for a profound description of the changes in the proton environment and for a TLS-analysis.

We performed a further diffraction experiments at high- T (660°C) with a Huber four-circle diffractometer (SV28/1) installed at the DIDO reactor – FZJ, with a furnace designed at the FZJ, using a crystal of natural epidote from the sample previously used (from the intrusive/metamorphic complex of Val Sissone, Retic Alps, Italy). A incident radiation (obtained using a Cu(200) single-crystal monochromator) with a constant wavelength of $0.87238(1)\text{\AA}$ was used. A total of 1230 unique reflections were recorded ($2\theta_{\text{max}} = 70^\circ$). The systematic extinction rules agreed with the space group $P2_1/m$. The structural refinement with the diffraction was performed in space group $P2_1/m$ at first with isotropic displacement parameters using the SHELXL-97 package (Sheldrick 1997), starting with the atomic coordinates of Kvik et al. (1988). The final least-square cycles were conducted with anisotropic thermal parameters and all the principal mean square atomic displacement parameters were positively defined.

The Al/Fe fraction at the M1, M2 and M3 octahedral sites was refined. At the end of the refinements, no peak larger than $\pm 0.90 \text{ fm}/\text{\AA}^3$ were found in the difference-Fourier map of the nuclear density. The final agreement index was $R_1(660^\circ\text{C}) = 0.0484$ for 126 refined parameters.

Neutron structural refinements allowed us to infer that the crystal structure of natural epidote is stable at least up to 660°C and no deoxydrilation effect occurs. At high- T we do not observe any statistically relevant difference of the cations distribution in the octahedral sites with respect to that observed at room- T . At present, we have no evidence of any T -induced order-disorder phenomena concerning the Al/Fe distribution in the M1-M2-M3 octahedral sites (the so called “non-convergent ordering”) or any high- T phase transition to lower symmetry due to Al/Fe “convergent ordering” on M3 (with a splitting of M3 into two sites: M3 and M3’, Franz & Liebscher 2004). The Fig.1 shows the major T -induced changes into the crystal structure of epidote on the basis of the structural refinements performed at room- T and at 660°C .

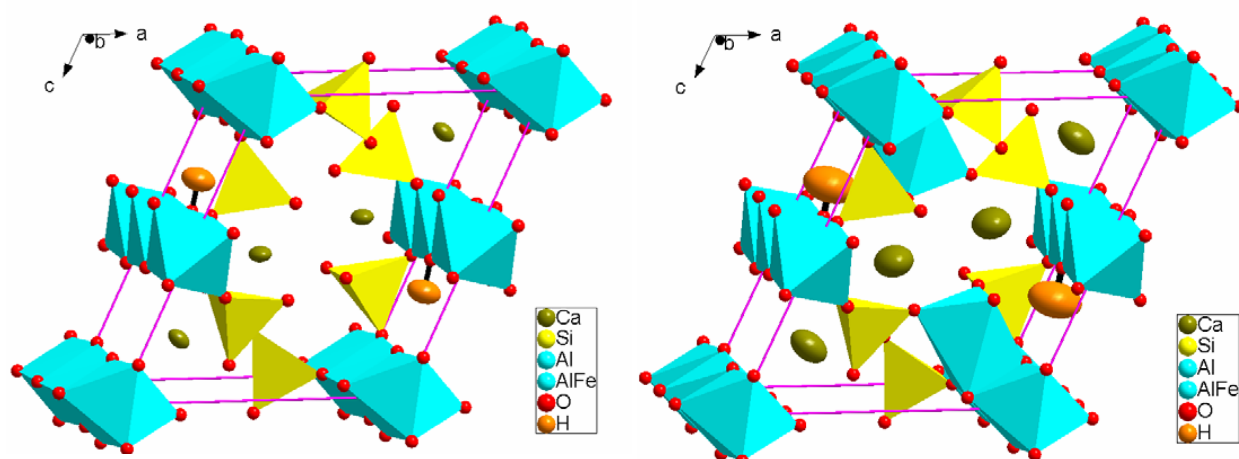


Fig. 1. Clinographic view of the crystal structure of topaz refined at room- T (left side) and at 660°C (right-side). Thermal ellipsoid probability: 99%.

References

- Kvick Å, Pluth JJ, Richardson Jr JW, Smith JV (1988) Acta Cryst B, 44, 351-355.
 Franz G, Liebscher A (2004) Rev. Min. Geoch., 56, 1-80.
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Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S28-06-002		
Experiment title:	Magnetic structure of TbMnO ₃		
Dates of experiment:	10.3.2006-13.3.2006	Date of report:	24.5.2006
Experimental team:			
Names:	Addresses:		
J. Voigt	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local contact:	A. Loose		

We have studied the magnetic structure of a TbMnO₃ single crystal by neutron diffraction. The compound has attracted considerable interest because it exhibits multiferroic behaviour. Antiferromagnetic order and the ferroelectric polarization are intimately connected as evidenced by the polarization flop from the *c*-direction to the *b*-direction in an applied magnetic field of several Tesla [1]. The formation of the ferroelectric polarization at $T_c = 28$ K seems to be coupled to a magnetic reorientation transition from a collinear incommensurate (IC) magnetic structure to a non-collinear. This transitions involves also a long range ordering of the Tb³⁺ ions according to a recent neutron diffraction study [2]. The transition temperature is significantly higher than temperature $T_{N,Tb} = 8$ K, at which the Tb moments order with a different propagation vector as compared to the ordering of the Mn subsystem.

Our recent resonant x-ray diffraction raised some doubt on the orientation of the Tb moment in the non collinear phase. According to Kenzelmann et al [2] the moment should be oriented along the crystallographic *a*-direction. The x-ray data gave some hints for an orientation along the *b*-direction, but the data were ambiguous. Hence we performed a single crystal study at temperatures $T = 10$ K, $T = 35$ K and $T = 50$ K using SV28 at a wavelength $\lambda = 0.87$ Å. The sample was mounted in a closed cycle refrigerator with a temperature range from 10 K to room temperature.

Fig 1 shows the integrated intensities for two series of reflections, normalised to the intensity of the (0 Δ 1) reflection. The full *a* component contributes to all reflections of type (0 Δ 1). For reflections of type (h Δ 1), the scattering vector becomes more parallel to the *a* component with increasing h.

The same holds for the $(0 \Delta 1)$ reflections considering the c component of the magnetic moment. The intensity should therefore decrease faster with respect to the $(0 \Delta 1)$ reflection at the respective temperature for both series of reflections, if either the a component or the c component is ordered. We observe the expected behaviour for the $(0 \Delta 1)$ series, but not for the $(h \Delta 1)$ series. However, since a scattering vector $(h \Delta 1)$ leads to an increased scattering from the c component (the scattering vector becomes more perpendicular to the c direction), the result is still not conclusive. The reflection $(0 1 - \Delta 1)$ was not observed, which could be due to the large background. It is particularly sensitive to the Tb moment [2]. Further data analysis is needed to test the published magnetic structure.

References

- [1] T. Kimura *et al.*, PHYSICAL REVIEW B **71**, 224425 (2005).
- [2] M. Kenzelmann *et al.*, PHYSICAL REVIEW LETTERS **95**, 087206 (2005).

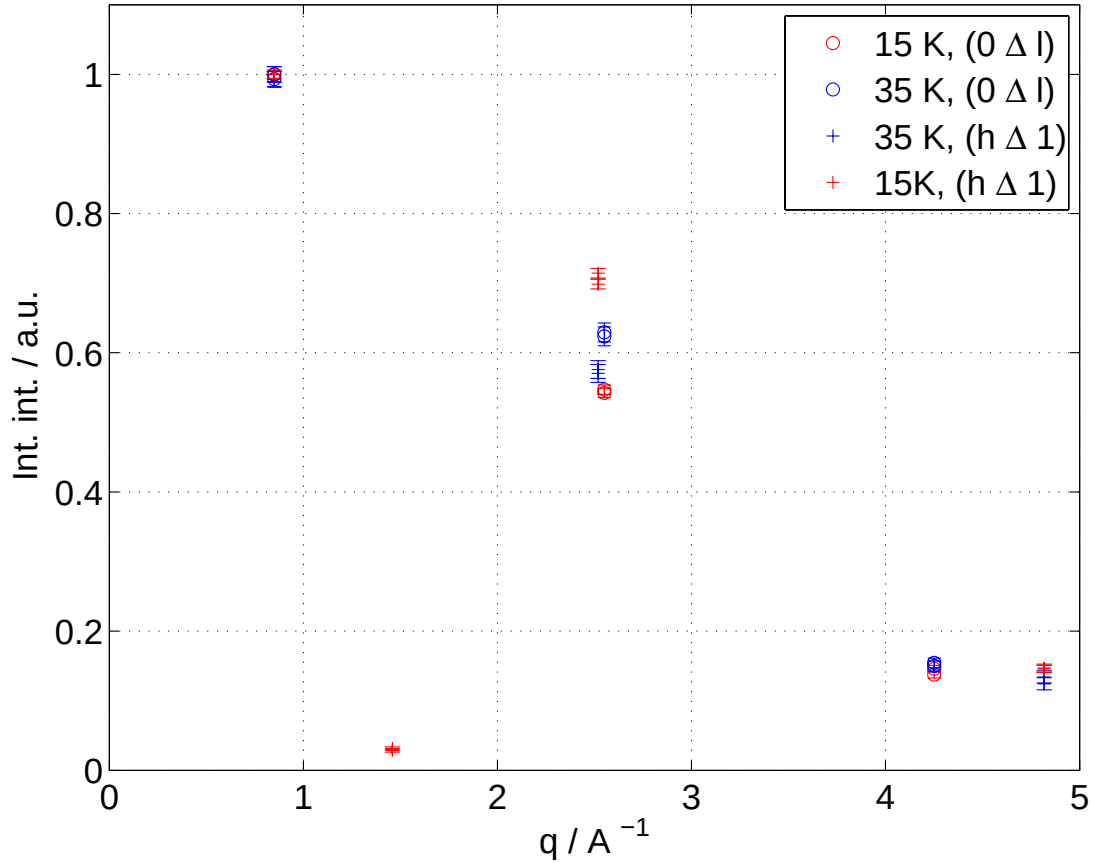


Fig. 1: Integrated intensities of reflections $(0 \Delta 1)$, $(0 \Delta 3)$, $(0 \Delta 5)$, $(0 \Delta 1)$, $(2 \Delta 1)$, $(4 \Delta 1)$, normalised to the intensity of the $(0 \Delta 1)$ reflection at the respective temperature.