1. Summary of Dissertation

1.1. Aim of dissertation

The aim of this thesis was to solve and describe the crystal structure of selected inorganic phosphates. Nine different compounds have been studied, including the NASICON type phosphates $Co_{0.5}Ti_2(PO_4)_3$, $Mn_{0.5}Ti_2(PO_4)_3$, $Na_{3.215}Fe_2(PO_4)_3$, the iron(II) diphosphate $Fe_2P_2O_7$ and hydrates of rare-earth hydrogen diphosphates $LnHP_2O_7{\cdot}3H_2O$ (Ln = Y, Tb, Dy, Yb) and $TbHP_2O_7{\cdot}4H_2O$. While NASICON type phosphates and rare-earth hydrogen diphosphates have a conventional three-dimensional crystal structure, the structure of α-$Fe_2P_2O_7$ is incommensurately modulated and has been described in (3+1)-dimensional superspace.

1.2. Overview of the content of dissertation

Dissertation is divided in six parts. Part 1 introduce the crystal structure analysis, the concept of aperiodic crystals and the superspace approach. Part 2 describes course of X-ray diffraction experiment and used experimental equipment. The next three parts, Part 3, Part 4 and Part 5, in which the structures of NASICON-type phospates, iron(II) diphosphate, and rare-earth hydrogen diphosphates are discussed, are the main parts of this work.

Part 1. Introduction and Initiation

• Chapter 2, **"Basic principles of crystal structure analysis"** concerns by fundamentals of crystal structure analysis, i.e. behaviour of X-rays, unit cell, symmetry, crystallographic systems and structure factor.

• Chapter 3, **"Twinning"** gives a brief overview of twinning in crystals"

• In chapter 4, **"Introduction to superspace",** the general concept of superspace is discussed, both in reciprocal and in direct space. The symbols of superspace groups and the symmetry in superspace are explained on an example.

Part 2. Experimental
Experimental equipment, the course of X-ray data collection, structure solution and refinement are described.

Part 3. Structure of NASICON phosphates
Crystal structure of three NASICON-type phosphates: $Mn_{0.5}Ti_2(PO_4)_3$, $Co_{0.5}Ti_2(PO_4)_3$, and $Na_{3.215}Fe_2(PO_4)_3$ is discussed.

Part 4. Crystal structure of iron(II) diphosphate
The procedures of treating an incommensurately one-dimensional modulated structure in (3+1)-dimensional superspace are presented. Non-modulated high temperature phase is described and the phase transition is discussed.

Part 5. Structure of rare earth hydrogen diphosphates.
Crystal structure of four isostructural trihydrates of rare earth hydrogen diphosphates. Crystal structure of terbium hydrogen diphosphate tetrahydrate.

Part 6. Conclusion, Perspectives and Outlook
Some possible carrying on for the here presented projects and ideas for future work are discussed.

1.3. Results and interpretation

1.3.1. Structure of NASICON phosphates

The general formula of NASICON-type materials is $M_xA_y(PO_4)_3$, where M can be a monovalent cation (Na^+, Li^+, Cu^+, ...) or a bivalent cation (Ca^{2+}, Ba^{2+}, Cu^{2+},...) and B is one or more ions in tri-, tetra-, or pentavalent state (Fe^{3+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Nb^{5+}, Sb^{5+}, ...).

Their crystal structure consists of heteropolyhedral $[A_y(PO_4)_3]$ framework built up by corner sharing $[AO_6]$ octahedra and $[PO_4]$ tetrahedra. M ions accomodate structural holes in the framework. There are two crystallographicaly different M sites, M1 and M2. While the M1 sites with sixfold coordination are situated berween two $[AO_6]$ octahedra, the M2 sites with eight to ten coordinating oxygens are located between the $[O_3AO_3M1O_3AO_3\ O_3AO_3M1]_\infty$ ribbons (Figure 1).

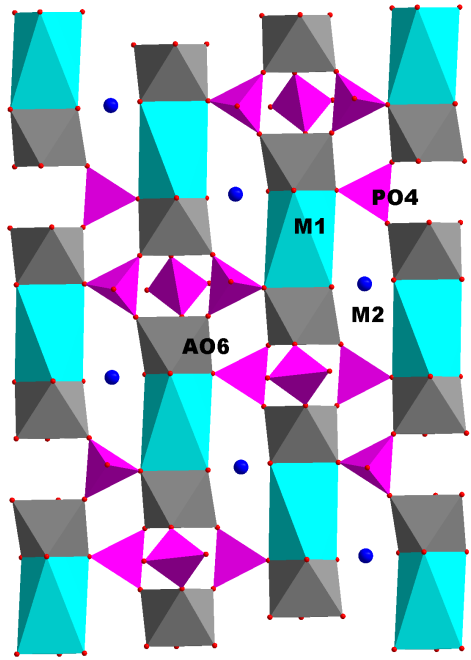
The structure is highly flexible and amenable to substitution on M, A or phosphorus sites to form a wide variety of isostructural materials. The M1 and M2 site occupancies may also be varied to form phases in which the number of M ions per formula lies between four and zero.

1.3.1.1. Crystal structure of $M_{0.5}Ti_2(PO_4)_3$ (M=Mn, Co)

The symmetry of the structure of $Mn_{0.5}Ti_2(PO_4)_3$ is represented by the space group $R\overline{3}$. The crystals were twinned by merohedry, the corresponding twinning matrix was

$$T = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

where $T = U_1^{-1}U_2$. U_1 and U_2 are orientation matrices of the first and the second twin domain, respectively.



1. NASICON-type structure

There are two crystallographically unique Ti^{4+} ions in the structure, both have a distorted octahedral coordination. Mn^{4+} ions fill one half of M1 sites. M1 site is split into two possible positions and Mn^{4+} occupy only one of them, leaving the other position free. Mn coordination polyhedron may be described as trigonal antiprism or a strongly irregular octahedron.

$Co_{0.5}Ti_2(PO_4)_3$ crystallizes in the $R\overline{3}c$ space group and its crystals exhibited pseudomerohedral twinning. The twinning matrix was

$$T = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Due to the higer symmetry of the structure, the M1 site is not split into two different position as in the structure $Mn_{0.5}Ti_2(PO_4)_3$. Co^{2+} ions occupy half of the M1 sites in a statistical way and the occupancy factor of Co is 0.5. Co adopts a trigonal antiprismatic configuration. The Ti^{4+} cation is in a distorted ocahedral environment of six oxygen atoms.

1.3.1.2. Structure of of $Na_{3.215}Fe_2(PO_4)_3$

The structure has been refined in space group $R\overline{3}c$ and corresponds to that of NASICON type phosphates. The heteropolyhedral framework is based on regular alternation of corner-sharing FeO_6 octahedra and PO_4 tetrahedra. The Na^+ cations are distributed over two crystallographic sites: the fully occupied six fold coordinated M1 site, and the eight-fold coordinated M2 site with occupancy factor 0.7383.

Fe is of mixed valence. The calculated bond valence sums[1] confirm that Fe1 site contains both Fe^{2+} and Fe^{3+} (2.795 (6)).

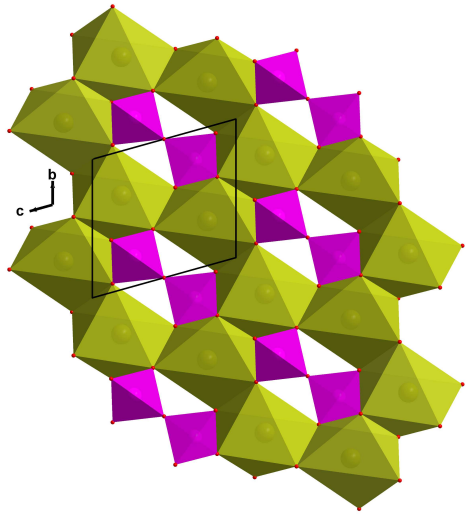
1.3.2. Crystal structure of iron(II) diphosphate

$Fe_2P_2O_7$ has an incommensurately modulated structure at ambient conditions. It undergoes a phase transition towards a non-modulated structure at $T_C = 365$ K.

The incommensurate structure has been solved by charge flipping method,[2,3] which yielded both the basic positions of the atoms and the shapes of their modulation functions. During the refinement, the modulation of the bridging oxygen of P_2O_7 group was described by a sawtooth function. The symmetry of the structure is described by superspace group $P\overline{1}(\alpha\beta\gamma)0$.

The average structure of iron(II) diphosphate can be considered as being built of honey comb-like layers of $Fe^{II}O3$ (Figure 2). Fe atom is coordinated by six oxygens forming a distorted octahedron; each [FeO6] octa-

hedron shares three edges with neighbouring octahedra to form the layer. The layers parallel with *bc* plane are connected by diphosphate groups located above the vacant position. The bridging oxygen of diphosphate group is situated at the centre of symmetry and therefore the P–O–P angle is 180 °.



2. Basic structure of $Fe_2P_2O_7$ viewed along *a*

The consequence of modulation is that instead of the centre of symmetry located in each three-dimensional unit cell there is only one global center of symmetry valid for the whole real space section. Thus atomic positions of the bridging oxygen can be distributed leading to various bent configurations of P_2O_7 groups.

The structure analysis shows that the modulation leads to a change of the coordination of the Fe^{2+} ions from distorted octahedra in the average structure towards a sixfold coordination in the form of a more regular

octahedron, a fivefold coordination in the form of square pyramid and various '5+1' coordinations.

The phase transition is primarily driven by dynamics of the diphosphate groups. In the high-temperature, thermally activated structure, the mismatch between the symmetry of P_2O_7 group and the global centrosymmetric symmetry (space group $P\overline{1}$) leads to a dynamic disorder of P_2O_7.[4]

1.3.3. Structure of rare-earth hydrogen diphosphates

1.3.3.3. Structure of $LnHP_2O_7 \cdot 3H_2O$, Ln = Dy, Tb, Y, Yb

The structure is built up of layers formed by hydrogen diphosphate groups and LnO8 (Ln = Y, Tb, Dy, Yb) polyhedra, stacked along the *c*-axis. Between these layers is located a disordered water molecule, being split into two partially occupied positions. Ln^{III} atom is eight-fold coordinated, sharing six oxygen atoms with four adjacent hydrogen diphosphate groups and two oxygen atoms with water molecules. The P–O–P bridging angles are 133.12 (12) °, 134.3 (2) °, 133.8 (2) ° and 132.7 (2) ° for Ln = Y, Tb, Dy and Yb, respectively. All the atoms are located on crystallographic general positions.

The layers are stabilized by O–H. . . O hydrogen bonds between coordinated water molecules and oxygens of hydrogen diphosphate groups. Proton of the hydrogen diphosphate is engaged in a strong hydrogen bond connecting two adjacent layers together. Oxygen atom of the disordered water molecule interacts with hydrogen atoms of coordinated water molecules in layers. Positions of hydrogen atoms of disordered water molecule could not be refined from X-ray data and their role in hydrogen bond framework is unknown.

1.3.3.4. Structure of $TbHP_2O_7.4H_2O$

The structure is made up of TbO_8 polyhedra and HP_2O_7 groups that form a three-dimensional network. In channels of the framwork running along *a* free water molecules are located. The Tb atom is coordinated by the O atoms of three symmetrically independent water molecules and by five O atoms belonging to four $HP_2O_7{}^{3-}$ anions. The bridging angle P–O–P between the two PO_4 tetrahedra is $130.73\,(11)\,^\circ$.

Network of TbO_8 and HP_2O_7 is additionally stabilized by O–H...O hydrogen bonding between coordinated water molecules and O atoms of the $HP_2O_7{}^{3-}$ anions. The hydrogen atom of the HP_2O_7 group is involved in a hydrogen bond with the oxygen atom of the free water molecule situated in the channels of structure framework. The hydrogen atoms of uncoordinated water interact with oxygen atom of surrounding hydrogen diphosphate groups.