Crystal Growth, Single-Crystal Structure Refinement and Unusual Ligand-Field Splittings of Lazulite-Type Oxidephosphates $MTi_2O_2(PO_4)_2$ (M = Fe^{II}, Co^{II}, Ni^{II})

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Dedicated to Professor Rudolf Hoppe on the Occasion of his 85th Birthday

Abstract. Single crystals of oxidephosphates $MTi_2O_2(PO_4)_2$ [M: Fe (dark red), Co (pinkish red), Ni (green)] with edge-lengths up to 0.4 mm were grown by chemical vapour transport. FeTi₂O₂(PO₄)₂ and CoTi₂O₂(PO₄)₂ are isotypic to NiTi₂O₂(PO₄)₂. The crystal structure of the latter was previously solved from powder data [FeTi₂O₂(PO₄)₂ (data for CoTi₂O₂(PO₄)₂ and NiTi₂O₂(PO₄)₂ in brackets): monoclinic, $P2_1/c$, Z = 2, a = 7.394(3) (7.381(6), 7.388(4)) Å, b = 7.396(2) (7.371(5), 7.334(10)) Å, c = 7.401(3) (7.366(6), 7.340(3)) Å, $\beta = 120.20(3)$ (120.26(6), 120.12(4))°, $R_1 = 0.0393$ (0.0309, 0.0539) wR₂ = 0.1154 (0.0740, 0.1389), 2160 (1059, 1564) independent reflections, 75 (76, 77) variables]. The single-crystal study allowed improved refinement using anisotropic displacement parameters, yielded lower standard deviations for the structural parameters and revealed a small amount of cation disordering. Twinning and cation disordering within the structures are

Introduction

The crystal structure of NiTi₂O₂(PO₄)₂ ("Ni_{0.5}TiPO₅" in [2]) has been solved and refined some years ago from X-ray powder diffraction data, in addition the electronic absorption spectrum (powder reflectance measurement) has been reported [2]. Only recently, structural data for FeTi₂₋ $O_2(PO_4)_2$ from powder data [3] and for two modifications of CuTi₂O₂(PO₄)₂ [4, 5] were published. These oxidephosphates belong to the Lipscombite/Lazulite structure family [6, 7]. Accomodation of various cations in different oxidation states and the possible substitution of O^{2-} by OH^{-} and H₂O illustrate the wide crystal chemical stability range of this structure type. Table 1 reviews phosphates of the Lipscombite/Lazulite family. The crystal chemical variability of this structure family demands for a structural systematization. Symmetry considerations on the basis of group-subgroup relations [8] provide a valuable tool for this purpose. Figure 1 shows the symmetry relation between the

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2568

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aristotype [9] of the Lipscombite/Lazulite structure family, tetragonal β -Fe₂O(PO₄) [10, 11, 12], and several ternary and polynary titanium phosphates. Occurence of disorder and twinning within the structures of this family are almost inevitable and can be linked to these symmetry relations. The particular unit cell dimensions found for oxide phosphates MTi₂O₂(PO₄)₂ lead to additional pseudomerohedral twinning which complicates single-crystal struc-

Table 1 Phosphates of the Lipscombite/Lazulite structure family. □ means octahedral void.

phosphate	Z	space group	reference
β -Fe ^{II/III} ₂ O(PO ₄); aristotype	4	I41/amd	[10, 11]
β -V ^{II/III} ₂ O(PO ₄)	4	I41/amd	[53]
Ni ^{II} Cr ^{III} O(PO ₄)	4	I41/amd	[11]
$\Box M^{II}Ti^{IV}_{2}O_{2}(PO_{4})_{2}$ (M: Fe, Co, Ni)	2	$P2_1/c$	[2], this paper
$\Box_2 Ti^{III}Ti^{IV}_{3}O_{3}(PO_4)_{3}$	24	F2dd	[54, 1]
$\Box_3 Ti^{IV} {}_5O_4(PO_4)_4$	4	$P2_{1}2_{1}2_{1}$	[54, 55, 56]
$\Box_{17} Cr^{III}_{4} Ti^{IV}_{27} O_{24} (PO_4)_{24}$	1	F2dd	[54]
$\Box V^{III}(H_2O)PO_4$	4	$P2_1/n$	[57]
$\Box_{0.385} V^{III}_{1.23} (OH)_{0.69} (H_2O)_{0.31} (PO_4) \cdot 0.33 H_2O$	4	I41/amd	[57]
$\Box Fe^{II}Fe^{III}_{2}(OH)_{2}(PO_{4})_{2}$	2	$P2_1/n$	[58, 59, 60]
$\Box Fe^{II}Al^{III}_{2}(OH)_{2}(PO_{4})_{2}$	2	$P2_1/n$	[58]
$\Box Mg^{II}Al^{III}_{2}(OH)_{2}(PO_{4})_{2}$	2	$P2_1/n$	[58]
$\Box Cu^{II}Fe^{III}_{2}(OH)_{2}(PO_{4})_{2}$	2	$P2_1/n$	[61]
$\Box Fe^{III}_{4}(OH)_{3}(PO_{4})_{3}$	4	C2/c	[62, 63]
$\Box_{2-x} Fe^{III}_{4-x} Fe^{II}_{3x} (OH)_{3-x} O_{3x} (PO_4)_3$	2	I41/amd	[64, 65]
$\Box Co_3(OH)_2(HPO_4)_2$	2	P21/c	[13, 66]



Fig. 1 Group-subgroup relations within the symmetry tree of the Lipscombite/Lazulite structure family.

ture refinements even more. Similar problems were encountered during structure determination and refinement of $Co_3(OH)_2(HPO_4)_2$ [13].

In addition to the crystallographic problems growth of single crystals of polynary phosphates is in general not an easy task. Even more demanding is crystallization of phosphates containing transition metals in rather low oxidation states like iron(II). In recent years we could show that the method of chemical vapour transport [14] is well suited for the crystallization of anhydrous (transition metal) phosphates [15, 16]. We therefore applied this technique to crystal growth of oxide phosphates $MTi_2O_2(PO_4)_2$ (M = Fe, Co, Ni, Cu, Zn).

The green colour of $NiTi_2O_2(PO_4)_2$ and the unusual UV/ vis spectrum reported in literature [2] are in marked contrast to yellow and orange colours observed for many other anhydrous nickel(II) phosphates [17]. Thus our interest in the ligand-field splitting experienced by the divalent cations in these structures was raised.

Experimental Section

Synthesis. Microcrystalline powders of $MTi_2O_2(PO_4)_2$ (M = Fe, Co, Ni) were obtained by isothermal heating in sealed silica tubes (3 days, 1000 °C) of equimolar amounts of finely ground TiP₂O₇,

 TiO_2 and MO (M: Co, Ni) (eq. (1)) or "FeO" (1/3 Fe₂O₃ + 2/3 Fe) (eq. (2)). TiP_2O_7 was prepared as described in [18]. The other starting materials were at least of p. a. grade. Their crystal chemical composition was checked by Guinier photographs.

$$TiP_2O_7 + TiO_2 + MO = MTi_2O_2(PO_4)_2$$
 (M: Co, Ni) (1)

$$3 \operatorname{TiP}_2 O_7 + 3 \operatorname{TiO}_2 + \operatorname{Fe}_2 O_3 + 2 \operatorname{Fe} = 3 \operatorname{FeTi}_2 O_2 (\operatorname{PO}_4)_2$$
(2)

Chemical vapour transport experiments for crystallisation and purification of the oxidephosphates $MTi_2O_2(PO_4)_2$ (M = Fe, Co, Ni) were carried out in sealed silica tubes (1 \sim 12 cm, d \sim 1.5 cm, $V \sim 21 \text{ cm}^3$), which were placed in the temperature gradient of electrically heated two-zone furnaces. Various transport agents were checked [chlorine (from in situ thermal decomposition of PtCl₂), mixtures H₂/HCl/(N₂) (from *in situ* thermal decomposition of NH₄Cl), HCl/(N₂) (from *in situ* thermal decomposition of stoichiometric amounts of PtCl2 and NH4Cl), mixtures I2/PI3/TiI4 (from in situ reaction of TiP with a surplus of iodine), and mixtures Cl₂/PCl₃/TiCl₄ (from in situ reaction of TiP with a surplus of chlorine)]. Generally, stoichiometric mixtures of TiP2O7, TiO2 and MO (M: Co, Ni) were used as starting materials. Experiments with separately synthesized oxidephosphates MTi₂O₂(PO₄)₂ as source materials did not show any siginificant differences in their transport behaviour. Conditions and results of representative experiments are summarized in Tables 2 to 4. Figure 2 shows crystals of the oxidephosphates obtained by CVT.

Table 2 Chemical vapour transport experiments for the crystallization of NiTi₂O₂(PO4)₂. Starting materials in all experiments: TiP₂O₇ (235.7 mg, 1.0617 mmol), TiO₂ (84.4 mg, 1.0617 mmol) und NiO (79.3 mg, 1.0617 mmol), TA: transport agent, $T_2 \rightarrow T_1$: temperature gradient, yield of crystals at the sink region of the ampoule: some mg (+), some crystals (~), few crystals (-).

TA / mg		$\begin{array}{c} T_2 \rightarrow T_1 \\ \textit{I} ^{\circ}C \end{array}$	t / d	products source	sink
PtCl ₂	30	$1000 \rightarrow 900$	7	NiTi ₂ O ₂ (PO ₄) ₂	no transport
PtCl ₂	50	$1000 \rightarrow 900$	9	$NiTi_2O_2(PO_4)_2$	no transport
PtCl ₂	50	$1000 \rightarrow 900$	7	$NiTi_2O_2(PO_4)_2$	no transport
NH ₄ Cl	5				*
NH ₄ Cl	15	$1000 \rightarrow 900$	7	NiTi ₂ O ₂ (PO ₄) ₂	$Ti_4P_6Si_2O_{25}$ (~)
					$NiTi_2O_2(PO_4)_2(-)$
I ₂	95	$1000 \rightarrow 900$	7	NiTi ₂ O ₂ (PO ₄) ₂	no transport
TiP	5				
PtCl ₂	100	$1000 \rightarrow 900$	7	$NiTi_2O_2(PO_4)_2$	$NiTi_2O_2(PO_4)_2(-)$
TiP	1.5				
PtCl ₂	100	$1000 \rightarrow 900$	7	NiTi ₂ O ₂ (PO ₄) ₂	$NiTi_2O_2(PO_4)_2(-)$
TiP	2.5				
PtCl ₂	100	$1060 \rightarrow 960$	14	$NiTi_2O_2(PO_4)_2$	$NiTi_2O_2(PO_4)_2(+)$
TiP	2.5				
PtCl ₂	100	$1060 \rightarrow 960$	4	NiTi ₂ O ₂ (PO ₄) ₂	$NiTi_2O_2(PO_4)_2(-)$
TiP	2.5				
PtCl ₂	100	$1020 \rightarrow 920$,	1	$NiTi_2O_2(PO_4)_2$	NiTi ₂ O ₂ (PO ₄) ₂ ^{a)}
TiP	2.5	$1000 \rightarrow 900$	3		
PtCl ₂	100	$1000 \rightarrow 900$	7	NiTi ₂ O ₂ (PO ₄) ₂	$NiTi_2O_2(PO_4)_2(+)$
TiP	5			α -SiO ₂	

^{a)} The crystal for the single-crystal data collection was selected from this experiment.

Table 3 Chemical vapour transport experiments for the crystallization of $CoTi_2O_2(PO_4)_2$. Starting materials in all experiments: TiP_2O_7 (235.6 mg, 1.0619 mmol), TiO_2 (84.4 mg, 1.0617 mmol) und CoO (79.6 mg, 1.0619 mmol), TA: transport agent, $T_2 \rightarrow T_1$: temperature gradient, yield of crystals at the sink region of the ampoule: some mg (+), some crystals (~), few crystals (-).

TA / mg		$\begin{array}{c} T_2 \rightarrow T_1 \\ I \ ^\circ C \end{array}$	t / d	products source	sink
PtCl ₂	55	$1000 \rightarrow 900$	7	CoTi ₂ O ₂ (PO ₄) ₂	no transport
PtCl ₂	55	$1060 \rightarrow 960$	10	CoTi ₂ O ₂ (PO ₄) ₂	$CoTi_2O_2(PO_4)_2(-)$
					$CoTi_4(PO_4)_6(+)$
					α -Co ₂ P ₂ O ₇ (+)
$PtCl_2$	105	$1040 \rightarrow 940$	7	$CoTi_2O_2(PO_4)_2$	$CoTi_2O_2(PO_4)_2(+)^{a, b}$
					$CoTi_4(PO_4)_6(-)$
PtCl ₂	100	$1040 \rightarrow 940$	7	$CoTi_2O_2(PO_4)_2$	$CoTi_4(PO_4)_6(+)$
					α -Co ₂ P ₂ O ₇ (+)
PtCl ₂	50	$1000 \rightarrow 900$	7	$CoTi_2O_2(PO_4)_2$	$CoTi_2O_2(PO_4)_2(-)$
NH ₄ Cl	5				$CoTi_4(PO_4)_6(+)$
					α -Co ₂ P ₂ O ₇ (~)
PtCl ₂	100	$1000 \rightarrow 900$	14	$CoTi_2O_2(PO_4)_2$	$CoTi_4(PO_4)_6(+)$
NH ₄ Cl	5			$CoTi_4(PO_4)_6$	α -Co ₂ P ₂ O ₇ (~)
NH ₄ Cl	15	$1000 \rightarrow 900$	14	$CoTi_2O_2(PO_4)_2$	$CoTi_4(PO_4)_6(+)$
_			_	$CoTi_4(PO_4)_6$	α -Co ₂ P ₂ O ₇ (-)
I ₂	95	$1000 \rightarrow 900$	7	$CoTi_2O_2(PO_4)_2$	$\operatorname{CoTi}_4(\operatorname{PO}_4)_6(+)$
TiP	5		_	$CoTi_4(PO_4)_6$	α -Co ₂ P ₂ O ₇ (~)
I ₂	100	$1000 \rightarrow 900$	7	$CoTi_2O_2(PO_4)_2$	$CoTi_4(PO_4)_6(+)$
TiP	1.5	4000 000	_	$CoTi_4(PO_4)_6$	α -Co ₂ P ₂ O ₇ (~)
PtCl ₂	100	$1000 \rightarrow 900$	7	$CoT_{12}O_2(PO_4)_2$	$CoT_{1_2}O_2(PO_4)_2$ (~)
TiP	1.5			$CoTi_4(PO_4)_6$ α -SiO ₂	

^{a)} The crystal suitable for the single-crystal data collection was selected from this batch.

^{b)} An excess of TiO₂ was added (5 mg).

Table 4 Chemical vapour transport experiments for the crystallization of FeTi₂O₂(PO4)₂. Starting materials in all experiments: TiP₂O₇ (237.34 mg, 1.07 mmol), TiO₂ (85.45 mg, 1.07 mmol), Fe (19.92 mg, 0.36 mmol) and Fe₂O₃ (56.96 mg, 0.36 mmol), TA: transport agent, $T_2 \rightarrow T_1$: temperature gradient, yield of crystals at the sink region of the ampoule: some mg (+), some crystals (~), few crystals (-).

TA / mg		$\begin{array}{c} T_2 \rightarrow T_1 \\ \textit{I} \ ^\circ C \end{array}$	t / d	products source	sink
NH ₄ Cl	30	$1000 \rightarrow 900$	7	FeTi ₂ O ₂ (PO ₄) ₂	FeTi ₄ (PO ₄) ₆ ($-$) Fe ₂ P ₂ O ₇ (\sim)
PtCl ₂ NH₄Cl	50 15	$1000 \rightarrow 900$	7	$FeTi_2O_2(PO_4)_2$ $FeTi_4(PO_4)_6$	$FeTi_4(PO_4)_6(-)$ $Fe_2P_2O_7(-)$
PtCl ₂ TiP	100 2.5	$1000 \rightarrow 900$	14	$\text{FeTi}_2\text{O}_2(\text{PO}_4)_2$	$\operatorname{FeTi}_2O_2(\operatorname{PO}_4)_2 \stackrel{\mathrm{a, b}}{}$
I ₂ TiP	95 05	$1000 \rightarrow 900$	7	FeTi ₂ O ₂ (PO ₄) ₂	no transport

 $^{\rm a)}$ The crystal for the single-crystal data collection was selected from this batch. $^{\rm b)}$ An excess of TiO₂ was added (5 mg).

By *EDX-analysis* the chemical composition of deposited crystals was confirmed (scanning tunneling microscope DMS 940, Zeiss Inc., equipped with an energy-dispersive spectrometer, EDAX Inc.). No incorporation of silicon into the phosphates was detected.

Single crystal electronic spectra of arbitrary faces of $MTi_2O_2(PO_4)_2$ (M = Fe, Co, Ni) crystals were measured at ambient temperature using a strongly modified CARY 17 microcrystal spectralphotometer (Spectra Services, ANU Canberra, Australia [19, 20]). The spectrometer allows measurement of polarised spectra of very small single-crystals with diameters down to 0.1 mm. Details on the spectrometer have already been described in literature [19, 20].

Guinier photographs using the image plate technique [21, 22] were taken for identification, examination of the powder samples for purity and for determination of lattice parameters. Details on this technique were reported in [23]. The lattice parameters were determined using the program SOS [24].

X-Ray single-crystal study. Intensity data were measured on a κ -CCD diffractometer (Enraf-Nonius Inc.) at ambient temperature. Structure determination and refinement were performed using the SHELX-97 [25] suite in the WinGX [26] framework. In addition the program KPLOT [27] was used to search for missing symmetry. Starting parameters for the single crystal structure refinements were obtained by Direct Methods assuming space group P1. This turned out to be necessary, because of twinning of most crystals, no reliable space-group determination was possible on the basis of systematic absences and statistics of intensity distribution. Thus, the metal and phosphorus atoms were revealed. Subsequent Δ -Fourier syntheses allowed localisation of the oxygen atoms. All atoms were refined allowing for anisotropic displacement parameters. Afterwards the search for higher symmetry was made using KPLOT. P2₁/c was found as possible space group in agreement with the structure model derived from x-ray powder data for NiTi2-O₂(PO₄)₂ [2]. After transformation of the lattice and the atomic parameters the twinnig law [1 0 0 0 -1 0 -1 0 -1] was introduced for $CoTi_2O_2(PO_4)_2$ and $NiTi_2O_2(PO_4)_2$. This twinning law was derived by group-subgroup considerations [8], relating the structures of the polynary oxidephosphates to that of the tetragonal aristotype β - $Fe_2O(PO_4)$ (Fig. 1). Fig. 4 visualizes the relation between the monoclinic unit cell and an orthorhombic F-lattice. A two-fold axis



Fig. 2 Crystals of oxidephosphates $MTi_2O_2(PO_4)_2$ [M: Fe (a), Co (b), Ni (c)] from chemical vapour transport experiments. Edgelengths up to 0.4 mm.

present in the orthorhombic structure is preserved as twin operation. For all three oxidephosphates remaining electron density at special postion 2d (site Fe2, at the centre of an octahedral void, sharing opposite faces with adjacent octahedra [TiO₆]; Fig. 6) and at general position 4e (site Ti2, close to the position of Ti1; Figure 6) indicated small amounts of disorder. Eventually, in the structure models partial occupancy of both positions 2a and 2d was assumed using the EADP constraint (SHELX-97) for both M²⁺ ions and restraining the sum for both positions to 1. Refinement of the iron compound without this restraint gave no hint on an occupancy lower than one, as a possible result of the presence of Fe^{III}. Additionally, disorder of Ti⁴⁺ among the two general positions Ti1



Fig. 3 Electronic single-crystal absorption spectra of oxidephosphates $MTi_2O_2(PO_4)_2$ (M: Fe, Co, Ni). The spectra are shifted along the ordinate axis for clarity. Hairlines are meant as an guide to the eye. Ticks (a, b, c, d) represent transition energies calculated within the AOM. The length of the ticks is proportional to the degree of triplett (for Ni^{II}) and quartet (for Co^{II}) character, respectively, of the corresponding excited state.



Fig. 4 Correlation between an orthorhombic F-centred unit cell (*Fddd*, a ~ 7.35 Å, b ~ 7.35 Å, c ~ 12.5 Å) and the monoclinic cell of the oxidephosphates MTi₂O₂(PO₄)₂ (M: Fe, Co, Ni; *P2*₁/*c*, a ~ 7.35 Å, b ~ 7.35 Å, c ~ 7.35 Å, β ~ 120°). The orthorhombic cell is related the unit cell of tetragonal β -Fe₂O(PO₄) (*I4*₁/amd, a = 5.344(5) Å, c = 12.460(8) Å) by the transformation matrix (1 -1 0 1 1 0 0 0 1) (Fig. 1).

and Ti2 (in one octahedral void) was introduced into the structure models. The resulting site occupation factors for M^{II} and Ti^{IV} refined independently to almost identical values, as expected from the disorder model (see "Discussion"). All refinements converged at reasonable residuals and crystal chemical parameters.

Information on crystal data, intensity measurement and structure refinement is summarized in Table 5. Final atomic coordinates, iso-



Fig. 5 Comparison of the crystal structures of tetragonal β -Fe₂O(PO₄) (a, b) and monoclinic oxidephosphates MTi₂O₂(PO₄)₂ (M: Fe, Co, Ni) (c, d).

Table 5 Crystal data for MTi₂O₂(PO₄)₂ (M: Fe, Co, Ni).

tropic displacement parameters and interatomic distances are given in Tables 6 and 7. Supplementary material has been deposited with Fachinformationszentrum Karlsruhe, Abt. IDNT, D-76344 Eggenstein-Leopoldshafen (e-mail: crysdata@fiz-karlsruhe.de) and can be obtained by contacting FIZ [reference numbers: CSD-418196 (FeTi₂O₂(PO₄)₂), CSD-418197 (CoTi₂O₂(PO₄)₂), CSD-418198 (NiTi₂O₂(PO₄)₂)].

Angular Overlap Modeling of $MTi_2O_2(PO_4)_2$ (M = Fe, Co, Ni)

Oxidephosphates MTi₂O₂(PO₄)₂ (M = Fe, Co, Ni) are containing trimeric units [M^{II}Ti^{IV}₂O₁₂] of three face-sharing octahedra (e. g. [Fe^{II}Ti^{IV}₂O₁₂] in Fig. 6). For the chromophores [M^{II}O₆] strong trigonal distortions with angles \angle (O,M^{II},O) ~ 79° and 101° are observed. For a better understanding of the correlation between angular distortion of the chromophores and their d-electron energies calculations within the framework of the *angular overlap model* (AOM) [38, 28, 29] were performed. An advantage of this model is its ability to use the chromophores with their actual geometry, as determined from crystal structure analysis. Instead of using global parameters, like 10Dq or Δ_0 , one σ - and two π -interactions (in total 18 bonding parameters for an octahedral chromophore) of each ligand with the five 3d-orbitals of the central ion are used for the fitting

Chemical Formula	FeTi ₂ O ₂ (PO ₄) ₂	$CoTi_2O_2(PO_4)_2$	NiTi ₂ O ₂ (PO ₄) ₂
Formula weight / $g \cdot mol^{-1}$	373.59	376.67	376.45
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Lattice parameters (from Guinier photographs)	• • •	• • •	• • • •
a/ Å	7.394(3)	7.381(6)	7.388(4)
b/ Å	7.396(2)	7.371(5)	7.334(10)
c/ Å	7.401(3)	7.366(6)	7.340(3)
b/ °	120.20(3)	120.26(6)	120.12(4)
Unit cell volume / Å ³	349.8(2)	346.2(5)	344.0(2)
Z	2	2	2
Absorp. coeff. / mm^{-1}	4.777	5.128	5.486
$D_{x-ray}/g \cdot cm^3$	3.547	3.614	3.635
Crystal colour	dark red	pinkish red	green
Crystal shape	prismatic	square disc	irregular-shaped isometric
Crystal size / mm ³	0.25 · 0.17 · 0.14	0.28.0.25.0.14	$0.17 \cdot 0.125 \cdot 0.12$
F(000)	360	362	364
Temperature [K]	293(2)	293(2)	293(2)
Wavelength (Mo-Ka, 0.71073 Å, graphite monoch	romator, k-CCD diffractometer (Nonius	s)	
Theta range / °	$3.18 \le \theta \le 39.95$	$3.18 \le \theta \le 30.04$	$3.18 \le \theta \le 35.05$
Absorption correction	multiscans,	multiscans,	Multiscans [68]
	within data reduction	within data reduction	after data reduction in
	using "Scalepack" [67]	using "Scalepack" [67]	WinGx [26]
Reflections collected	4195	4010	14618
Independent reflections	2160 [R(int) = 0.020]	1059 [R(int) = 0.037]	1564[R(int) = 0.053]
Index ranges	$-13 \le h \le 13$	$-10 \le h \le 10$	$-11 \le h \le 11$
("whole sphere")	$-13 \le k \le 13$	$-10 \le k \le 10$	$-11 \le k \le 11$
	$-13 \le l \le 13$	$-10 \le l \le 10$	$-11 \le l \le 11$
Parameters	75	76	77
R indices $[I > 2\sigma(I)]$	$R_1 = 0.039$	$R_1 = 0.031$	$R_1 = 0.054$
	$wR_2 = 0.116$	$wR_2 = 0.074$	$wR_2 = 0.138$
R indices (all data)	$R_1 = 0.042$	$R_1 = 0.032$	$R_1 = 0.056$
	$wR_2 = 0.117$	$wR_2 = 0.075$	$wR_2 = 0.143$
Goodness-of-fit on F^2	1.301	1.224	1.235
BASF	single-crystal	0.046(1)	0.472(3)
Weighting scheme	A = 0.0398, B = 1.5798	A = 0.0056, B = 2.2109	A = 0.0001, B = 8.2246
Extinction coefficient	_	_	0.002(2)
Largest diff. peak and hole / $e \cdot Å^{-3}$	1.878 and -1.377	0.848 and -0.798	2.183 and -1.460



Fig. 6 Trimer [Fe^{II}Ti^{IV}₂O₁₂]. Ellipsoids are given at the 90 % probability level.

between calculated and observed transition energies. This decomposition of the global ligand field parameter (10Dq or Δ_0) into parameters describing individual bonding interactions permits also accounting for second-sphere ligand field effects [30], e. g. cation-cation interaction. To reduce the number of independent bonding parameters, constraints between some of them were introduced. Thus, for the energy e_{σ} (M^{II}-O), proportionality to the distance d(M-O)^{-5.0} is assumed [38, 31]. In general, the energy of e_{π} is set to one quarter of the corresponding energy e_{σ} in the case of "undisturbed" π -interaction [15, 38]. In the case of the particular bonding situation encountered in the oxidephosphates $e_{\pi} \sim 0$ has been assumed. The validity of this assumption will be discussed.

Interelectronic repulsion is introduced into the AOM calculations via the Racah parameters B and C, spin orbit coupling by ξ . For the angular overlap modelling the free ion ratios $C_0/B_0 = 4.3$ (Fe^{II}), 3.9 (Co^{II}), and 4.3 (Ni^{II}) were used and retained during the calculations [38]. Variations in the covalency of the M-O interaction in the complexes were considered by variable nephelauxetic ratios β [β = B/B₀; $B_0 = 897 \text{ cm}^{-1}$ (Fe^{II}), 989 cm⁻¹ (Co^{II}), 1042 (Ni^{II})] [38].

Table 6 Atomic coordinates und isotropic displacement parameters of a) NiTi₂O₂(PO₄)₂ (Rietveld-Refinement [2]), b) NiTi₂O₂(PO₄)₂ (single-crystal refinement, this work), c) $CoTi_2O_2(PO_4)_2$, d) $FeTi_2O_2(PO_4)_2$.

Atom		Position	x	у	z	s.o.f	U _{eq} [Å ²] ^{a)}
M1	a	2 <i>a</i>	0	0	0	1	0.005
	b	2a	0	0	0	0.898(3)	0.0067(3)
	с	2a	0	0	0	0.9799(19)	0.0071(2)
	d	2a	0	0	0	0.9724(16)	0.0079(1)
M2 ^{b)}	а	2d	_	_	-	_	_
	b	2d	1/2	0	1/2	0.102(3)	0.0067(3)
	с	2d	1/2	0	1/2	0.0201(19)	0.0071(2)
	d	2d	1/2	0	1/2	0.0276(16)	0.0079(1)
Ti1	а	4e	0.7348(5)	0.2203(5)	0.5301(5)	1	0.006
	b	4e	0.7352(2)	0.2215(2)	0.5291(2)	0.912(4)	0.0064(3)
	с	4e	0.7334(1)	0.2215(1)	0.5296(1)	0.9799(24)	0.0055(2)
	d	4e	0.7340(1)	0.2227(1)	0.5290(1)	0.9753(16)	0.0063(1)
Ti2 ^{b)}	а	4e	-	-	-	-	
	b	4e	0.7650(2)	0.2780(2)	0.4820(2)	0.088(4)	0.0064(3)
	с	4e	0.7567(48)	0.2774(50)	0.4741(51)	0.0201(24)	0.0055(2)
	d	4e	0.7640(30)	0.2740(20)	0.4780(30)	0.0247(16)	0.0063(1)
Р	а	4e	0.2462(9)	0.1237(9)	0.7508(8)	1	0.008
	b	4e	0.2464(2)	0.1238(2)	0.7502(2)	1	0.0041(3)
	с	4e	0.2458(1)	0.1224(1)	0.7488(1)	1	0.0044(2)
	d	4e	0.2471(1)	0.1213(1)	0.7483(1)	1	0.0055(1)
O1	а	4e	0.7640(2)	0.1589(2)	0.7671(2)	1	0.003
	b	4e	0.7640(9)	0.1528(6)	0.7648(7)	1	0.0113(9)
	с	4e	0.7623(4)	0.1559(4)	0.7663(4)	1	0.0089(5)
	d	4e	0.7612(3)	0.1574(3)	0.7634(3)	1	0.0103(3)
O2	а	4e	0.7766(2)	0.0031(2)	0.0939(2)	1	0.005
	b	4e	0.7863(8)	0.0013(8)	0.1003(7)	1	0.0106(8)
	с	4e	0.7823(4)	0.0051(4)	0.1004(4)	1	0.0090(4)
	d	4e	0.7793(3)	0.0049(2)	0.1002(3)	1	0.0097(3)
O3	а	4e	0.4400(2)	0.2415(2)	0.8716(2)	1	0.003
	b	4e	0.4426(8)	0.2389(8)	0.8745(8)	1	0.0129(9)
	с	4e	0.4399(4)	0.2392(4)	0.8695(4)	1	0.0103(5)
	d	4e	0.4404(3)	0.2390(3)	0.8669(3)	1	0.0109(3)
O4	а	4e	0.2579(2)	0.0086(2)	0.5816(2)	1	0.005
	b	4e	0.2673(9)	0.0099(8)	0.5883(8)	1	0.0147(10)
	с	4e	0.2615(4)	0.0097(4)	0.5834(4)	1	0.0108(5)
	d	4e	0.1614(3)	0.0087(3)	0.5835(3)	1	0.0113(3)
O5	а	4 <i>e</i>	0.0578(2)	0.2481(2)	0.1452(2)	1	0.004
	b	4e	0.0564(8)	0.2491(8)	0.1423(8)	1	0.0142(9)
	с	4e	0.0543(4)	0.2515(4)	0.1438(4)	1	0.0087(5)
	d	4 <i>e</i>	0.0560(3)	0.2530(2)	0.1444(3)	1	0.0093(3)

^{a)} $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i \cdot a_j$ ^{b)} In the refinement of NiTi₂O₂(PO₄)₂ from powder data [2] no disorder of the metal cations was allowed for.

Table 7 MTi₂O₂(PO₄)₂ (M: Fe, Co, Ni). Interatomic distances / Å in trimers [M^{II}Ti₂O₁₂] and in [PO₄] groups. Distances are given only for the mainly occupied sites M1 and Ti1.

FeTi ₂ O ₂ (PO ₄) ₂		CoTi ₂ O ₂ (PO	$(4)_2 NiTi_2O_2(PO_4)_2$)2
[Fe1O ₆]		[Co1O6]		[Ni1O ₆]	
Fe1-O1 (2x)	2.105(2)	Co-O1 (2x)	2.078(3)	Nil-O1 (2x)	2.063(5)
Fe1-O2 (2x)	2.105(2)	Co-O2 (2x)	2.080(3)	Ni1-O2 (2x)	2.050(5)
Fe1-O5 (2x)	2.091(2)	Co-O5 (2x)	2.072(3)	Ni1-O5 (2x)	2.041(5)
[Ti1O ₆]		[Ti1O ₆]		[Ti1O ₆]	
Til-Ol	1.713(2)	Til-Ol	1.717(3)	Til-Ol	1.709(5)
Ti1-O1	2.255(2)	Til-O1	2.245(3)	Til-O1	2.253(5)
Ti1-O2	2.067(2)	Til-O2	2.067(3)	Ti1-O2	2.086(6)
Ti1-O3	1.901(2)	Til-O3	1.895(3)	Ti1-O3	1.893(5)
Til-O4	1.910(2)	Til-O4	1.905(3)	Til-O4	1.899(6)
Til-O5	2.094(2)	Til-O5	2.086(3)	Til-O5	2.094(6)
Fe1-Ti1	2.923(1)	Col-Til	2.927(2)	Nil-Til	2.909(2)
[PO ₄]		[PO ₄]		[PO ₄]	
P1-O2	1.545(2)	P1-O2	1.546(3)	P1-O2	1.540(5)
P1-O3	1.519(2)	P1-O3	1.517(3)	P1-O3	1.522(5)
P1-O4	1.524(2)	P1-O4	1.526(3)	P1-O4	1.523(5)
P1-O5	1.536(2)	P1-O5	1.535(3)	P1-O5	1.533(5)

The spin-orbit coupling parameter ξ was also assumed to be reduced relative to the free ion values (ξ_0 (Fe^{II}) =

2573

400 cm⁻¹, $\xi_0(\text{Co}^{\text{II}}) = 515 \text{ cm}^{-1}$, $\xi_0(\text{Ni}^{\text{II}}) = 630 \text{ cm}^{-1}$) according to β .

For the AOM calculations the PC program CAMMAG [32, 33] in a modified version [34] was used. Best fit AOM parameters for the spectra of $NiTi_2O_2(PO_4)_2$ and $CoTi_2O_2(PO_4)_2$ are summarised in Table 8.

Table 8 Summary of ligand-field parameters for Fe^{II} , Co^{II} , and Ni^{II} in oxidephosphates $MTi_2O_2(PO_4)_2$.

	Fe	Со	Ni
Racah parameters for the free ions [38]			
B_0 / cm^{-1}	897	989	1042
C_0 / cm^{-1}	3857	4253	4585
C/B	4.3	4.3	4.4
ξ_0 / cm^{-1}	400	515	630
Tanabe-Sugano evaluation			
$\Delta_0 / \mathrm{cm}^{-1}$	9660 a)	8030	7800
B / cm^{-1}	—	895	925
$\beta = \mathbf{B}/\mathbf{B}_0$	_	0.90	0.89
Angular overlap modelling ^{b)}			
$e_{\sigma,max}$ (M-O) / cm^{-1}	—	2875	2850
$e_{\sigma,norm}(M-O)_{2,0}^{c)} / cm^{-1}$	—	3620	3420
e_{σ} (M-Ti) / cm ⁻¹	—	-500	-500
B / cm^{-1}	—	811	854
$\beta = B/B_0$	-	0.82	0.82

^{a)} Calculated from the barycentre of the band around 9900 cm⁻¹, assuming for the ${}^{5}T_{2g}$ ground state a splitting, which is one quarter of the observed splitting of the excited ${}^{5}E_{g}$ state.

^{b)} σ -interactions between M and oxygen were chosen according to previous investigations [17, 40, 41], they were assumed to be proportional to $d(M-O)^{-5.0}$. π -interactions were neglected ($e_{\pi} = 0 \text{ cm}^{-1}$), see "Discussion"; ξ was reduced relative to ξ_0 as B to B₀, the ratios C/B of the free ions were kept during the modelling.

^{c)} σ -interaction between M and oxygen normalized to d(M-O) = 2.00 Å, using the relation $e_{\sigma} \sim d(M-O)^{-5.0}$ [31].

As a first step the transition energies in the spectrum of $NiTi_2O_2(PO_4)_2$ were modelled. Using $e_{\sigma,max}(Ni-O) =$ 3000 cm^{-1} (for the shortest observed, Tab. 7, distance $d(Ni-O) = 2.041 \text{ Å} \text{ and } e_{\sigma}(Ni-O_i) \sim d(Ni-O_i)^{-5.0}),$ e_{π} (Ni-O) = 0 cm⁻¹, and B = 875 cm⁻¹ (C/B = 4.4, β = 0.84, $\xi = 529 \text{ cm}^{-1}$) allowed a reasonable fit (Fig. 3a) to bands \tilde{v}_1 and \tilde{v}_2 . Even the rather large splitting of \tilde{v}_2 was reproduced. For \tilde{v}_3 , however, this calculation leads to a splitting of ca. 2500 cm^{-1} , which is not in accordance with the observed spectrum (Fig. 3). Searching for an improved match differences in the σ -interaction of Ni^{II} with oxide and oxygen of a phosphate group were considered. This clearly changed the fit, especially in the magnitude of the band splittings, to the worse (Fig 3b). Eventually, weak interactions with σ -symmetry ($e_{\sigma} = -500 \text{ cm}^{-1}$) between Ni^{II} and adjacent Ti^{IV} were assumed. In other words, the Ti^{IV} cations were considered as additional ligands of Ni^{II}. Doing so led to a nice match of all observed spectral features $(e_{\sigma,max}(Ni-O) = 2850 \text{ cm}^{-1}, B = 854 \text{ cm}^{-1}, C/B = 4.4, \beta =$ 0.82, $\xi = 517 \text{ cm}^{-1}$; Fig. 3c).

Using for **CoTi₂O₂(PO₄)**₂ the same bonding model $(e_{\sigma,max}(\text{Co-O}) = 2875 \text{ cm}^{-1}, e_{\sigma} (\text{Co-Ti}) = -500 \text{ cm}^{-1}, \text{B} = 811 \text{ cm}^{-1}, \text{C/B} = 4.3, \beta = 0.82, \xi = 422 \text{ cm}^{-1};$ Fig. 3d) immediately gave a very good match with the observed

spectrum. Neglecting e_{σ} (Co-Ti) allows also a fit to the observed band energies, which was, however, less good.

Angular overlap modelling on the basis of the bonding model derived for the nickel(II) and cobalt(II) oxidephosphate did not allow a reasonable fit to the absorption bands observed for $FeTi_2O_2(PO_4)_2$. In particular the rather large band splittings due to low-symmetry ligand-fields were not reproduced by the calculations. We attribute this failure to the presence of a dynamic Jahn-Teller effect (see Discussion).

Results and Discussion

Chemical vapour transport

The CVT experiments allow crystallization of oxidephosphates MTi₂O₂(PO₄)₂ (M^{II}: Fe, Co, Ni), although the observed deposition rates are rather low (a few mg/d). Migration of these phosphates proceeds always from the higher to the lower temperature $(T_2 \rightarrow T_1)$ due to endothermic reactions. Gaseous mixtures of Cl₂, PCl₃, and TiCl₄ (molar ratio 0.26 : 0.03 : 0.03; from *in situ* reaction of TiP with a surplus of PtCl₂) are in general suitable as transport agent for the oxidephosphates, even though such mixtures do also attack the wall of the silica tube. For $NiTi_2O_2(PO_4)_2$ no other transport agent allowed controlled crystallisation. For $CoTi_2O_2(PO_4)_2$ plain chlorine, too, used as transport agent, leads to a migration of the oxidephosphate via the gas phase. Transport experiments aiming at the crystallisation of CoTi₂O₂(PO₄)₂ or FeTi₂O₂(PO₄)₂ led under various experimental conditions to formation and chemical vapour transport of NASICON [35, 36] type phosphates M^{II}Ti₄(PO₄)₆ [M: Fe (orange-red), Co (lavender colour)]. This is apparently one of the very rare cases, where crystals of NASICON type compounds suitable for a single-crystal structure investigation were obtained. Detailed crystallographic investigations on these phosphates are in progress [1].

Using plain chlorine (from *in situ* decomposition of PtCl₂) for CVT of CoTi₂O₂(PO₄)₂, CoCl_{2,g}, TiCl_{4,g}, O_{2,g}, and P₄O_{10,g} are expected as volatile species (eq. (3)). The dominance of gaseous P₄O₁₀ as phosphorus carrier under such conditions has already been discussed [15, 16]. The corresponding equilibrium with NiTi₂O₂(PO₄)₂ is apparently thermodynamically less favourable and does not allow volatilization of the phosphate. FeTi₂O₂(PO₄)₂, on the other hand, is oxidized by chlorine in a quantitative reaction (eq. (4)), leading to the formation of Fe^{III}₄Ti^{IV}₂₇O₂₄(PO₄)_{24,s}, Fe₂O_{3,s}, FePO_{4,s}, and FeCl_{3,g}.

$$CoTi_{2}O_{2}(PO_{4})_{2,s} + 5 Cl_{2,g} = CoCl_{2,g} + 2 TiCl_{4,g} + 1/2 P_{4}O_{10,g} + 5/2 O_{2,g} (3)$$

27 FeTi_{2}O_{2}(PO_{4})_{2,s} + 27/2 Cl_{2,g} = 2 Fe_{4}Ti_{27}O_{24}(PO_{4})_{24,s}
+ 2 Fe_{2}O_{3,s} + 6 FePO_{4,s} + 9 FeCl_{3,g} (4)

Addition of a few mg TiP to chlorine prevents oxidation of iron(II)-oxidephosphate and creates favourable transport conditions (low oxygen equilibrium pressures) for all oxidephosphates. Mixtures $Cl_{2,g}/PCl_{3,g}$ (from oxidation of TiP by chlorine) are strongly chlorinating reagents. Their applicability for chemical vapour transport of lanthanum monophosphate LaPO₄ has been pointed out by *Schäfer*, almost 40 years ago [37]. Eq. (5) is likely to be the dominating transport reaction under these conditions.

$$\begin{split} MTi_2O_2(PO_4)_{2,s} + 2 & Cl_{2,g} + 2 & PCl_{3,g} = MCl_{2,g} \\ &+ 2 & TiCl_{4,g} + P_4O_{10,g} & (M: Fe, Co, Ni) \end{split}$$
(5)

It is worth noting that most transport experiments with $FeTi_2O_2(PO_4)_2$ and $CoTi_2O_2(PO_4)_2$ led to the formation of additional phosphates $[M_2P_2O_7, MTi_4(PO_4)_6; M:$ Fe, Co; Table 3 and 4] in the equilibrium solids. This observation points to an incongruent gasphase solubility for $FeTi_2$. $O_2(PO_4)_2$ and $CoTi_2O_2(PO_4)_2$, with an accumulation of titanium as tetrachloride in the gas phase, while MO and P_4O_{10} are enriched in the solid phase (eq. (6)). Consequently, a small surplus of TiO₂ in the starting mixture avoids formation of the neighbouring phosphates (Table 3).

$$5 \text{ MTi}_{2}\text{O}_{2}(\text{PO}_{4})_{2,s} + 12 \text{ Cl}_{2,g} = 2 \text{ M}_{2}\text{P}_{2}\text{O}_{7,s} + \text{ MTi}_{4}(\text{PO}_{4})_{6,s} + 6 \text{ TiCl}_{4,g} + 6 \text{ O}_{2,g} (\text{M: Fe, Co}) \quad (6)$$

In our experiments the new iron(III)-oxidephosphate $Fe^{III}_{4}Ti^{IV}_{27}O_{24}(PO_4)_{24,s}$ (isotypic to $M^{III}_{4}Ti^{IV}_{27}O_{24}(PO_4)_{24,s}$ (M: Ti, Cr) [54, 56]) and NASICON type phosphates $Fe^{II}Ti^{IV}_{4}(PO_4)_6$ and $Co^{II}Ti^{IV}_{4}(PO_4)_6$ were obtained for the first time as single crystals suitable for detailed structural studies. Such investigations are in progress [1].

Crystal Structure

The oxidephosphates MTi₂O₂(PO₄)₂ (M^{II}: Fe, Co, Ni) are members of the Lipscombite/Lazulite structure family (Fig. 4, 5). Their crystal structure can be derived from that of tetragonal β -Fe₂O(PO₄), which is the aristotype of this structure family. β -Fe₂O(PO₄) crystallizes in space group $I4_1/amd$ (a = 5.344(5) Å, c = 12.460(8) Å, Z = 4) [10, 11]. Its structure is built up by chains of face-sharing octahedra [Fe^{II/III}O₆] along the [1 0 0] and [0 1 0] directions (Fig. 5a and b). Each octahedron shares four vertices with [PO₄] tetrahedra. The two remaining vertices are occupied by oxide ions, which crosslink the chains. The oxide ions are coordinated by four iron cations while the oxygen atoms of phosphate groups are connected to two iron cations (and phosphorus; c.n.(O) = 3; Fig. 4).

Figs. 4 and 5 illustrate the relationship between the structures of β -Fe₂O(PO₄) and MTi₂O₂(PO₄)₂. In β -Fe₂O(PO₄) all octahedral voids are occupied by iron. Substitution of Fe^{II/III} by M^{II}/Ti^{IV} leads to an ordered introduction of vacancies into the chains of face-sharing octahedra, which is accompanied by a reduction of symmetry from space group *I*4₁/*and* to *P*2₁/ *c* (a ~ 7.3 Å, b ~ 7.3 Å, c ~ 7.4 Å, $\beta \sim 120^\circ$, Z = 2). In the ideal structure of MTi₂O₂(PO₄)₂ the occupancy sequence for the octahedral voids is ..., Ti⁴⁺, M^{II}, Ti^{IV}, \Box , ... thus the main structural motif are trimers [M^{II}Ti^{IV}₂O₁₂] (Fig. 6). In the real structure the empty sites "□" are to a small extend (up to 10 %) occupied by M^{II} (site M2, Wyckoff position 2*d*), as is revealed by our single crystal X-ray investigations (Table 6). The disorder of the M^{II} cations causes in their immediate vicinity a relaxation of the lattice. Titanium(IV) is shifted due to the electronic repulsion between M^{II} and Ti^{IV} to split position Ti2. Another consequence of the electrostatic repulsion between M^{II} and Ti^{IV} cations within the trimers [M^{II}Ti₂O₁₂] are strong trigonal distortions of the coordination polyhedra [M^{II}O₆] (point group D_{3d}) and [Ti^{IV}O₆] (point group C_{3v}) (Tables 7; Fig. 6). In contrast to β-Fe₂O(PO₄) the coordination of the oxide ions is reduced to c.n.(O) = 3, oxygen atoms of phosphate groups are connected to one (O3, O4) or two metal cations (O2, O5).

Group theoretical considerations of the β -Fe₂O(PO₄) and MTi₂O₂(PO₄)₂ structures elucidate their close relation. The lattice parameters and the atomic coordinates derived from the aristotype β -Fe₂O(PO₄) for the MTi₂O₂(PO₄)₂ structures by group-subgroup considerations are consistent with those obtained from the single crystal X-ray investigations (Fig. 7). The translationsgleiche transition of index 2 from space group Fddd (crystal class 2/m 2/m 2/m) to C2/c (crystal class 2/m) means loss of a two-fold axis parallel the b-axis in the lattice of the supergroup. This symmetry operation is conserved as the twinning element, meaning a two-fold twin-axis along the a-axis of the subgroup. The klassengleiche transition of index 2 from space group C2/c to $P2_1/c$ leads to a splitting of the Wyckhoff position 4cinto two different positions 2a and 2d with the same site symmetry and the same chemical environment. Such a situation causes frequently disorder, as it is indeed observed for cations M^{II}.

Colour and electronic absorption spectra

Crystals of FeTi₂O₂(PO₄)₂ are deeply red (Fig. 2a). The absorption spectrum (Fig. 3a) shows a broad band in the nir region with two maxima at 8700 cm^{-1} and 11000 cm^{-1} . The red color results from rather low-lying charge-transfer transitions, that block all light above 16500 cm⁻¹. Crystals of $CoTi_2O_2(PO_4)_2$ are light red with a pinkish tint (Fig. 2b). Three broad absorption bands at $\tilde{v}_1 = 8100 \text{ cm}^{-1}$, $\tilde{v}_2 =$ 15600 cm⁻¹, and $\tilde{v}_3 = 19500$ cm⁻¹ (with a maximum at 18900 cm^{-1} and a shoulder at 20400 cm^{-1}) are observed (Fig 3b). Evaluation of the spectrum using the Tanabe-Sugano diagram in ref. [38] led for the chromophore $[Co^{II}O_6]$ to the ligand-field splitting $\Delta_0 = 8030 \text{ cm}^{-1}$ and the Racah parameter $B = 895 \text{ cm}^{-1}$ ($\beta = B/B_{\text{free ion}} = 0.90$). Crystals of $NiTi_2O_2(PO_4)_2$ are light green (Fig. 2c). Three strong absorption bands at $\tilde{v}_1 = 8000 \text{ cm}^{-1}$, $\tilde{v}_2 =$ 13400 cm⁻¹, and $\tilde{v}_3 = 24000$ cm⁻¹ are found (Fig. 3c). The band around 13400 cm⁻¹ appears to be very broad, possibly with three components (a, b, c) at 12000, 13400 and 14600 cm^{-1} . The band around 24000 cm^{-1} shows a maximum at 24700 cm^{-1} and a shoulder at 23600 cm^{-1} , but is still rather narrow. At about 21000 cm^{-1} a weak band,



Fig. 7 Group-subgroup relation between the crystal structures of β -Fe₂O(PO₄) and FeTi₂O₂(PO₄)₂.

possibly originating from a spin-forbidden electronic transition is observed. The observed spectrum is very similar, however better resolved than the one reported in [2]. Based on the baricentres of the three broad bands at 8000, 13500, and 24000 cm⁻¹ an evaluation according to *Tanabe* and *Sugano* leads for the chromophore [Ni^{II}O₆] to $\Delta_o = 7832$ cm⁻¹ and B = 926 cm⁻¹ ($\beta = B/B_{free ion} = 0.89$).

The colours of oxide-phosphates $MTi_2O_2(PO_4)_2$ (M = Fe (deep-red), Co (pinkish-red), Ni (green)) differ considerably from those of other anhydrous phosphates containing these cations (iron(II) phosphates: colourless [39], cobalt(II) phosphates: purple to violett colour [40], nickel(II) phosphates: orange to yellow [17, 41, 42]). In the case of $FeTi_2O_2(PO_4)_2$ the deep-red colour clearly is not the result of d-d electronic transitions, which are observed in the nearinfrared region. Apparently, the colour originates from some sort of charge-transfer transition. Comparison with $CoTi_2O_2(PO_4)_2$ and $NiTi_2O_2(PO_4)_2$ suggests that LMCT($O^{-II} \rightarrow Ti^{IV}$) transitions should be at higher energy than the observed 16500 cm⁻¹. This points to the possibil-ity of IVCT transitions (Fe^{II} \rightarrow Ti^{IV} and/or Fe^{II} \rightarrow Fe^{III}).

In comparison to other anhydrous nickel(II) phosphates (e. g. NiP₄O₁₁ and CaNiP₂O₇ [41]) and many chromophores containing Ni2+ ions in undistorted octahedral environment, the spectrum of NiTi₂O₂(PO₄)₂ shows three distinct differences. Firstly, the ligand-field splitting $\Delta(\text{NiTi}_2\text{O}_2(\text{PO}_4)_2) = 7800 \text{ cm}^{-1}$ is roughly 1000 cm⁻¹ higher than the splittings observed for NiP_4O_{11} or CaNiP₂O₇. The splitting ($\sim 2500 \text{ cm}^{-1}$) of the second spinallowed transition (\tilde{v}_2 in Fig. 3) is significantly larger and, thirdly, the interelectronic repulsion parameters are smaller than in other anhydrous nickel(II) phosphates. As shown in Fig. 3c angular overlap modelling allows a good fit to these pecularities. In addition, the same bonding model gives with almost identical parameters a perfect match to the spectrum observed for CoTi₂O₂(PO₄)₂ (Fig. 3d). The obtained best-fit AOM parameters are in good agreement with parameters derived for large series of nickel and cobalt phosphates [17, 40]. According to the AO modelling the particular bonding situation of Ni^{II} (and Co^{II}) in the trimers [M^{II}Ti^{IV}₂O₁₂] is characterized by several geometric and electronic consequences of the close vicinity between Ti^{IV} and M^{II}. a) Face-sharing of octahedra [Ti^{IV}O₆] and [M^{II}O₆] leads to strong radial and angular distortion of the latter. b) Ti⁴⁺ (d⁰ system) is strongly π -accepting, thus leaving no electron density at the bridging oxygen atoms for π interaction with the d-orbitals of the nickel ions. The exclusive presence of σ -donating oxygen ligands without any π donating effect explains the rather large ligand-field splitting. Similar observations have been reported for Ni^{II}-containing perowskites (e. g. Sr₂Ni^{II}M^{VI}O₆, M^{VI}: W, Te), where d⁰-cations in the vicinity of Ni^{II} lead to a dramatically higher ligand-field splitting in the [Ni^{II}O₆] chromophores than d¹⁰-cations like Te^{VI} [43]. c) The angular distortion of the chromophore [Ni^{II}O₆] together with the weak interaction between Ti^{IV} and Ni^{II} accounts for the large splitting of the second absorption band. d) This same interaction allows also weak delocalization of d-electron density from Ni^{II} to Ti^{IV}, similar to the situation already described for Cr^{III} doped into Ga₂O₃ or Al₂O₃ [44].

Obviously, the rather simple AOM approach allows a nice description of the fairly complex bonding situation encountered by Ni^{II} and Co^{II} in the oxidephosphates MTi₂O₂(PO₄)₂ (M: Co, Ni). Even second-sphere ligand field effects [30] like direct MII-TiIV interaction and reduced π -bonding are well accounted for. Considering the detailed understanding for the bonding situation of Ni^{II} and Co^{II} in the oxidephosphates, it was quite disappointing, however, not unexpected, that the d-d electronic transitions observed for $\text{FeTi}_2\text{O}_2(\text{PO}_4)_2$ (Fig. 3) and α -CuTi₂O₂(PO₄)₂ ($\tilde{\nu}_1 =$ 7940 cm⁻¹, $\tilde{v}_2 = 10240$ cm⁻¹, and $\tilde{v}_3 = 12640$ cm⁻¹ [4]) could not be matched by calculations within the AOM framework.

Allowing within the AOM framework for the static geometric distortions (radial and angular) of the chromophore $[Fe^{II}O_6]$ and introduction of second-sphere ligand field effects reduces the symmetry of the ligand field from O_h to D_{3d} . According to group theory, such a symmetry reduction does not cause a splitting of the excited electronic ${}^{5}E_{g}$ state for iron(II). Results of AOM calculations $[e_{\sigma,max}(Fe-O)] =$ 3400 cm^{-1} , B = 736 cm⁻¹, C/B = 4.3, β = 0.82, ξ = 328 cm⁻¹, parameters in analogy to the nickel(II) and cobalt(II) oxidephosphate] are in agreement with this expectation. They lead to $\tilde{v}({}^5T_{2g} \rightarrow {}^5E_g) = 9900 \text{ cm}^{-1}$, with a splitting of the ${}^{5}E_{g}$ state of only some 200 cm⁻¹, due to spin-orbit coupling and marginal deviation from the idealized symmetry. A match of the observed splitting of the excited ${}^{5}E_{g}$ state ($\delta \sim 2400 \text{ cm}^{-1}$, Fig. 3) is only obtained in AOM calculations, if one assumes an additional tetragonal distortion of the ligand field experienced by the Fe²⁺ ions $[4 \text{ x } e_{\sigma,eq}(\text{Fe-O}) = 3735 \text{ cm}^{-1}, 2 \text{ x } e_{\sigma,ax}(\text{Fe-O}) = 2470 \text{ cm}^{-1},$ B = 736 cm⁻¹, C/B = 4.3, β = 0.82, ξ = 328 cm⁻¹]. Such a distortion as consequence of differences in the bonding interactions between iron(II) and oxide and iron(II) and oxygen from a phosphate group, respectively, is in clear contradiction to the modelling of the spectra of $NiTi_2O_2(PO_4)_2$ and $CoTi_2O_2(PO_4)_2$. For d⁶ and d⁹ ions like iron(II) and copper(II), however, such a splitting might be caused by the presence of a dynamic Jahn-Teller effect [45]. Many examples are known in literature for vibronic coupling in Fe^{II} and Cu^{II} containing chromophores as an explanation for largely split absorption bands, despite highly symmetrical coordination polyhedra (e. g. $Fe(H_2O)_6^{2+}$ [46], KFeF₃ [47], $Cu(H_2O)_6^{2+}$ [48], CuF_6^{4-} [49]). With $e_{\sigma,max}(Fe-O) =$ 3400 cm^{-1} at $d_{min}(\text{Fe-O}) = 2.090 \text{ Å}$ (Tab. 7) for the dynamically undistorted chromophore and $e_{\sigma,eq}(Fe-O) =$ 3735 cm^{-1} and $e_{\sigma,ax}(\text{Fe-O}) = 2470 \text{ cm}^{-1}$ for the dynamically distorted chromophore one may estimate using the relation $e_{\sigma}(Fe^{II}-O) \sim d(Fe-O)^{-5.0}$ a dynamically elongated distortion with $d_{eq}(Fe-O) = 2.05 \text{ Å}$ and $d_{ax}(Fe-O) =$ 2.22 Å. These distances obtained for the vibronically distorted chromophore [Fe^{II}O₆] in FeTi₂O₂(PO₄)₂ coincide nicely with those observed for statically distorted polyhedra $[Fe^{II}O_6]$ in FeP₄O₁₁ [50], Fe₂P₄O₁₂ [51], and Fe₃(PO₄)₂ [52]. Our considerations do not allow to distinguish between vibronic tetragonal elongation and compression nor do they provide exclusive evidence for the tetragonal distortion along the direction iron(II)-oxide. However, we believe that such a vibronic distortion is the most reasonable.

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