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Crystal structure of $FePO_4$ at 294 and 20 K

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Abstract. $FePO_4$ was obtained by reaction of Fe_2O_3 with H_3PO_4 at 5 kP, and 520 K, and subsequent dehydration at 750 K. The structure is isotype to $AlPO_4$-quartz (berlinite). The structure was investigated by neutron scattering of a powder sample.

1. Introduction

It was well-known that $FePO_4$ has a quartz-type structure. However, the structure was not yet determined [1]. The interest arose owing to the large difference of the size of the cations and the few structures with FeO_4 tetrahedra.

2. Experimental

An amorphous powder of $FePO_4 \cdot H_2O$ was obtained by the reaction of Fe_3O_4 with highly concentrated H_3PO_4 in a teflon vessel at 520 K and 5 kP for a few days. The amorphous powder obtained was dehydrated at 750 K and a powder of $FePO_4$ quartz-type structure was obtained. The powder was investigated by using a powder diffractometer at the reactor FR2 of the Kernforschungszentrum Karlsruhe. Several measurements were performed at room temperature and at 20 K. The refinement of the structure was performed with the help of a Rietveld program modified by Hewat [2]. The following scattering factors of the elements were used: Fe 0.916; P 0.513; and O 0.0583×10^{-12} cm as given by Koester et al. [3]. The experimental details are summarized in Table 1.

Table 1. Crystal data and details of structure determination.

Temperature [K]	294	20
Space group	$P3_121$	$P3_121$
Formula units per unit cell	3	3
Lattice constants [Å]	$a = 5.028(1)$	$a = 5.019(1)$
(Standard deviations)	$c = 11.235(2)$	$c = 11.226(2)$
$d_{(\mathrm{calc})}$ [g · cm^{-2}]	1.841	1.850
Wavelength [Å]	1.0156	1.0156
2 θ range [°]	10–104	10–82.8
Number of independent reflections	420	252
$R_{\mathrm{iso}}(\mathrm{I})$[a] [%]	12.03	11.35
$R_{\mathrm{iso}}(\mathrm{Y})$[b] [%]	15.63	15.69
$R_{\mathrm{iso}}(\mathrm{wY})$[c] [%]	17.85	20.24

[a] $R_{\mathrm{iso}}(\mathrm{I})$ R-value for the individual reflections using isotropic temperature factors.

[b] $R_{\mathrm{iso}}(\mathrm{Y})$ R-value for the total intensity distribution.

[c] $R_{\mathrm{iso}}(\mathrm{wY})$ R-value for the intensity distribution using weighted intensities. The weight is determined by the counting statistics and the errors occurring with the correction of the background.

Table 2. Atomic coordinates and thermal parameter. (Standard deviations are given in parentheses).

Temperature [K]		294	20
Fe (3a)	x	0.449(1)	0.452(2)
	y	0	0
	z	1/3	1/3
	B	0.51(7)	0.5(1)
P (3b)	x	0.478(2)	0.464(3)
	y	0	0
	z	5/6	5/6
	B	0.3(1)	0.02(2)
O(1) 6(c)	x	0.423(3)	0.418(3)
	y	0.311(2)	0.317(2)
	z	0.3975(6)	0.3955(6)
	B	1.8(1)	0.2(1)
O(2) 6(c)	x	0.409(3)	0.403(3)
	y	0.267(2)	0.364(2)
	z	0.8756(7)	0.8727(9)
	B	1.4(1)	0.4(2)

Origin of space group as in International Tables for X-ray Crystallography since 1952.

3. Discussion

The structure determination confirmed the isotypy of $FePO_4$ to $AlPO_4$-quartz which was recently refined by Ngo Thong et al. [4]. The final parameters are given in Table 2. The interatomic distances and angles are

Table 3. Interatomic distances [Å] and bond angles [°]. (Standard deviations are given in parentheses.)

Temperature [K]	294	20	Temperature [K]	294	20
FeO_4-tetrahedron			PO_4-tetrahedron		
Fe–O(1) 2 ×	1.793(3)	1.821(3)	P–O(1) 2 ×	1.469(5)	1.517(4)
Fe–O(2) 2 ×	1.866(5)	1.889(6)	P–O(2) 2 ×	1.606(5)	1.559(3)
O(1)–O(1)	3.08(1)	3.419(3)	O(1)–O(1)	2.492(3)	2.507(3)
O(1)–O(2) 2 ×	2.993(9)	3.048(9)	O(1)–O(2) 2 ×	2.508(9)	2.529(8)
O(1)–O(2) 2 ×	2.890(2)	2.938(4)	O(1)–O(2) 2 ×	2.514(2)	2.519(3)
O(2)–O(2)	3.067(3)	3.05(1)	O(2)–O(2)	2.507(9)	2.458(9)
O(1)–Fw–O(1)	118.1(6)	116.0(6)	O(1)–P–O(1)	116.0(2)	111.4(2)
O(1)–Fe–O(2) 2 ×	109.8(5)	110.5(5)	O(1)–P–O(2) 2 ×	109.1(6)	110.6(5)
O(1)–Fe–O(2) 2 ×	104.4(3)	104.7(3)	O(1)–P–O(2) 2 ×	109.6(3)	109.9(4)
O(2)–Fe–O(2)	110.5(3)	110.5(2)	O(2)–P–O(2)	102.6(9)	104.1(7)
Rotation angle of tetrahedra against basis plane			Intertetrahedral bonds		
FeO_4	18(3)	20(3)	Fe–O(1)–P	142.7(2)	139.4(2)
PO_4	22(3)	25(3)	Fe–O(2)–P	134.9(3)	133.7(3)

given in Table 3. At low temperatures the tilt of the tetrahedra with respect to the (001)-plane is increased, i.e. the difference to the high-temperature phase above 980 K is enlarged. By lowering the temperature the Fe–O–P bond angles are reduced. At low temperatures the tetrahedra, especially the FeO_4 one, become more and more regular. Indications of a magnetic structure have not been found. Similar structures have been recently investigated by Goiffon et al. [5].

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