Single Crystal Structure of the Divalent Europium Chloroapatite $Eu_5(PO_4)_3Cl$

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The chloroapatite $Eu_5(PO_4)_3Cl$ has been synthesized by a solid-state reaction route using a salt flux. Its structure has been solved and refined from single crystal X-ray data: apatite type, $P6_3/m$, a = 988.36(4), c = 720.32(3) pm, Z = 2, $R(F)$ = 0.021 and $wR(F^2)$ = 0.063 for 748 unique reflections and 40 variables. The $Eu_5(PO_4)_3Cl$ structure contains isolated $(PO_4)^{3-}$ tetrahedra and two crystallographically independent divalent europium sites. The $Eu1^{2+}$ ion at the $4f$ position is located in a distorted tri-capped trigonal prism whereas the $Eu2^{2+}$ ion at the $6h$ position is located in a strongly distorted square anti-prism. The chloride ions have octahedral europium coordination (307 pm Eu–Cl).

Key words: Oxophosphate, Europium Compound, Crystal Structure, Apatite

Introduction

ZrCuSiAs-type phosphide oxides *RET*PO (*RE* = rare earth element; T = late transition metal) have intensively been studied in the last 15 years with respect to their magnetic, optical, and superconducting properties [1, and refs. therein]. This field underwent a true renaissance in 2006 when superconductivity was discovered in LaFePO ($T_C \approx 3.5 – 7$ K) [2, 3] and LaNiPO ($T_C = 4.5$ K) [4, 5]. Besides the reports on superconductivity, the knowledge on physical properties of these materials is scarce, although more than 40 of the quaternary phosphide oxides are known [1].

The *RE*ZnPO series [6 – 8] has thoroughly been studied for the magnetic and optical properties. Interestingly, CeZnPO and PrZnPO are dimorphic [7]. The cerium compounds Ce*T*PO (T = Fe, Ru, Os) contain stable trivalent cerium [9, 10]. CeFePO is a magnetically non-ordered heavy Fermion metal, CeRuPO is a rare example of a ferromagnetic (T_C = 15 K) Kondo lattice system, and CeOsPO orders antiferromagnetically at T_N = 4.5 K. The so far highest ordering temperatures have been observed for UCuPO [11] and LaMnPO [12, 13].

We have recently started a systematic study of the magnetic properties of the *RET*PO phosphide oxides and broadly used NaCl / KCl fluxes as reaction and crystal growth media. So far no pnictide oxides are known with trivalent europium. Instead, some of our samples resulted in well-shaped crystals of the chloroapatite $Eu_5(PO_4)_3Cl$. The structure of $Eu_5(PO_4)_3Cl$ had so far only been characterized on the basis of powder X-ray diffraction data [14]. Herein we report on crystal growth studies and a precise single crystal structure refinement.

Experimental Section

Synthesis

First hints at the phosphate chlorides were obtained during attempts to synthesize ZrCuSiAs materials with europium. The title compound was then prepared by a solid-state reaction from a mixture of red phosphorus (Hoechst, Knapsack, ultrapure), Eu_2O_3 (Molycorp, > 99.99 %) and a (1 : 1 molar ratio) NaCl (Merck, > 99.5 %) / KCl (Chempur, 99.9 %) salt flux with 1 : 3 : 6 molar ratio, respectively. The mixture was put in an alumina tube, which was sealed under vacuum in a silica tube. To insure consumption of the phosphorus and to avoid its sublimation, the tube was heated at 500 °C for 24 h and then heated at 850 °C for 72 h. By a relatively fast decrease of the temperature at a rate of 20 °C/h to r. t., we obtained yellow and white crystals of $Eu_5(PO_4)_3Cl$ and Eu_2O_3, respectively. The flux was dissolved with demineralized water.

EDX data

Semiquantitative EDX analyses of many crystals including the one investigated on the diffractometer (Fig. 1) were carried out with a Leica 420i scanning electron microscope with EuF_3, GaP, and KCl as standards. The experimentally observed composition was close to the ideal one. Traces of sodium potassium aluminum compounds due to the reactivity of the alumina tube with the salt flux were observed on the surface of some crystals.

X-Ray diffraction

The polycrystalline sample obtained by crushing some of the flux-grown crystals was characterized by a Guinier

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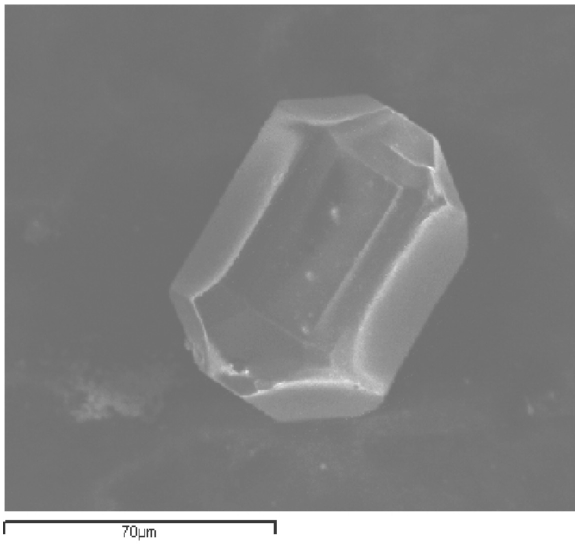

Fig. 1. Scanning electron micrograph of the $Eu_5(PO_4)_3Cl$ single crystal used for the XR data collection.

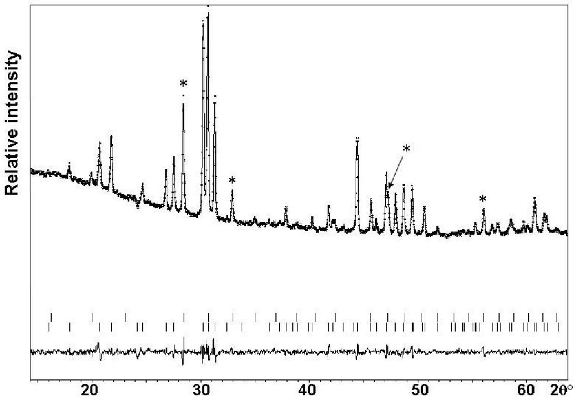

Fig. 2. Observed, calculated and difference plots for the XRPD profile refinement of the $Eu_5(PO_4)_3Cl$ sample obtained from flux synthesis. The peak positions of the phase Eu_2O_3 are indicated by asterisks.

pattern (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 4.9130, c = 5.4046 Å) as an internal standard. Taking the presence of two phases ($Eu_5(PO_4)_3Cl$ and Eu_2O_3) into account, a full pattern matching refinement was performed with the JANA2006 program package [15]. The background was estimated by a Legendre function, and the peak shapes were described by a pseudo-Voigt function. This allowed us to confirm the biphasic mixture of the sample (Fig. 2). The refined lattice parameters (Table 1) are in agreement with the data (a = 9.886(3), c = 7.187(2) Å) published by Mayer *et al.* [14].

Table 1. Crystallographic data and structure refinement for $Eu_5(PO_4)_3Cl$.

Formula	$Eu_5(PO_4)_3Cl$
Crystal color	yellow
MW, g mol^{-1}	1080.2
Crystal system	hexagonal
Space group	$P6_3/m$
Lattice parameters:	
a, Å	9.8836(4)
c, Å	7.2032(3)
Cell volume, Å^3	V = 609.4
Z	2
Density calcd., g cm^{-3}	5.88
Crystal shape	block
Temperature, K	293(1)
Diffractometer	Stoe IPDS II
Monochromator	oriented graphite
Radiation; λ, pm	MoK_α; 71.073
Scan mode	multi-scan
$h\ k\ l$ range	±14; ±14; ±10
$\theta_{min}/\theta_{max}$, deg	2.38 / 31.92
Linear absorption coeff., mm^{-1}	26.0
Absorption correction	Gaussian
T_{min}/T_{max}	0.197 / 0.323
No. of reflections	22087
R_{int}	0.047
No. of independent reflections	748
Reflections used [$I \geq 3\sigma(I)$]	661
Refinement technique	F^2
F(000), e	946
R factors $R(F)/wR(F^2)$	0.021 / 0.063
No. of refined parameters	40
G.o.f.	1.23
Weighting scheme	$w = 1/(\sigma^2(I) + 0.0016I^2)$
Diff. Fourier residues (max. / min.), e$^-$ Å^{-3}	−1.57 / +2.62

Table 2. Atom positions and isotropic displacement parameters (Å^2) for $Eu_5(PO_4)_3Cl$.

Atom	Site	x	y	z	U_{eq}
Eu1	4f	2/3	1/3	0.00131(5)	0.0071(1)
Eu2	6h	0.01044(3)	0.25703(3)	3/4	0.0068(1)
P	6h	0.03424(15)	0.40695(15)	1/4	0.0043(5)
Cl	2b	0	0	0	0.0112(6)
O1	6h	0.8558(5)	0.3369(6)	1/4	0.0096(16)
O2	6h	0.1185(6)	0.5865(5)	1/4	0.0109(15)
O3	12i	0.0888(4)	0.3566(5)	0.4227(5)	0.0123(12)

A crystal suitable for single crystal X-ray diffraction was selected on the basis of the size and the sharpness of the diffraction spots in Laue photographs obtained on a Buerger camera (using white Mo radiation). The data collection was carried out on a Stoe IPDS II diffractometer using MoK_α radiation. Data processing and all refinements were performed with the JANA2006 program package [15]. A Gaussian-type absorption correction was applied, and the shape of the crystal was determined with the video microscope of the Stoe CCD camera. Details about the data collection and crystallographic parameters are summarized in Table 1.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu1	0.00820(15)	U_{11}	0.00476(15)	0.00410(7)	0	0
Eu2	0.00750(15)	0.00746(16)	0.00580(17)	0.00393(11)	0	0
P	0.0043(6)	0.0054(6)	0.0029(6)	0.0023(5)	0	0
Cl	0.0104(6)	U_{11}	0.0127(12)	0.0052(3)	0	0
O1	0.0038(18)	0.014(2)	0.010(2)	0.0038(15)	0	0
O2	0.013(2)	0.0024(17)	0.015(2)	0.0012(15)	0	0
O3	0.0134(15)	0.0213(16)	0.0065(15)	0.0120(14)	0.0022(12)	0.0062(13)

Table 3. Anisotropic displacement parameters (Å^2) for Eu$_5$(PO$_4$)$_3$Cl. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$.

	Distance	BV		Distance	BV
Eu1–O3(×3)	2.854(3)	0.141	P–O3(×2)	1.535(4)	1.248
Eu1–O2(×3)	2.594(4)	0.285	P–O2	1.538(5)	1.238
Eu1–O1(×3)	2.577(4)	0.299	P–O1	1.539(5)	1.235
	⟨2.675⟩	BVS [6] = 1.752		⟨1.537⟩	BVS = 4.98
		BVS [9] = 2.175			
Eu2–O3(×2)	2.522(4)	0.347		Angle	
Eu2–O3(×2)	2.702(5)	0.213	O3–P–O3	108.3(3)	
Eu2–O2	2.447(7)	0.425	O3–P–O2	107.4(2)	
Eu2–O1	2.858(5)	0.140	O3–P–O1	111.3(2)	
	⟨2.625⟩	BVS [6] = 1.685	O2–P–O1	110.9(4)	
Eu2–Cl(×2)	3.073(3)	0.230		⟨109.5⟩	
		BVS [8] = 1.915			

Table 4. Interatomic distances (Å), angles (deg) and bond valence sums (BVS, with coordination numbers in brackets) for Eu$_5$(PO$_4$)$_3$Cl. Average distance and angle values are given in brackets.

BV = $e^{(r_0-r)/b}$ with the following parameters: b = 0.37, r_0 (Eu^{II}–O) = 2.13, r_0 (P^{V}–O) = 1.617, and r_0 (Eu^{II}–Cl) = 2.53 Å [23, 24].

Structure refinement

The extinction conditions observed for the Eu$_5$(PO$_4$)$_3$Cl crystal agree with the space group $P6_3/m$, in accordance with recently published data on isotypic Sr$_5$(PO$_4$)$_3$Cl [16]. The heavy atom positions were localized using the superflip program implemented in the JANA2006 package [15]. The use of difference Fourier synthesis allowed us to localize the oxygen atom positions. With anisotropic displacement parameters for all positions, the residual factors converged to the values listed in Table 1. Refinement of the Eu1 and Eu2 occupancies showed no deviations from the ideal values. The refined atomic positions and anisotropic displacement parameters (ADPs) are given in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420546.

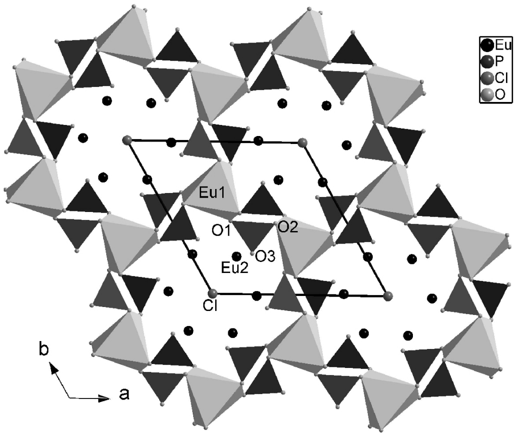

Fig. 3. A [001] projection of the structure of the chloroapatite Eu$_5$(PO$_4$)$_3$Cl.

Discussion

The crystal chemical details of the apatite structure have repeatedly been reviewed [17 – 19]. Here we give only a brief description of the Eu$_5$(PO$_4$)$_3$Cl structure. As emphasized in Fig. 3, the structure is composed of different interconnected polyhedra. The Eu1 atoms have coordination number 9. Six oxygen atoms build up a slightly twisted (twist angle 18.9°) trigonal prism which is capped on each rectangular face by additional oxygen atoms of the [PO$_4$] tetrahedra. The Eu2 atoms have the slightly smaller coordination number 8 with six oxygen and two chlorine atoms in their coordination sphere. The average Eu–O distances of Eu1 and Eu2 are similar (Table 4). They compare well with the Eu–O distance of 257 pm in NaCl-type EuO [20] and that of the divalent europium ions in Eu$_3$O$_4$ (264 – 296 pm) [21], while the trivalent europium ions in that oxide have significantly smaller Eu–O distances in the ranges 230 – 239 and 224 – 243 pm. The bond valence sums (BVS [22, 23], Table 4) of both europium sites in Eu$_5$(PO$_4$)$_3$Cl are also in agreement with divalent europium, as was already evident from the ^{151}Eu Mössbauer data reported in [14].

The corners of the Eu1O$_6$ trigonal prisms are connected to six [PO$_4$] tetrahedra. These are quite regular with an average P–O distance of 1.537 Å. This is consistent with the value 1.55 Å estimated from the effective ionic radii of four-coordinated P^{5+} and O^{2-} [22]. The corresponding calculated BVS value of 4.98 is in very good agreement with the expected 5+ value [23].

The chloride anions are located on the *c* axis. They are coordinated by six Eu2^{2+} cations in the form of slightly distorted octahedra (4.31 Å Eu2–Eu2 within triangles, and 4.37 Å Eu2–Eu2 between these triangles). The octahedra are condensed *via* common triangular faces along *c*.

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