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Apatite-type $Pr_9K(SiO_4)_6O_2$—a potential oxide ion conductor

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Abstract

$Pr_9K(SiO_4)_6O_2$ (hexagonal, $P6_3/m$ (No. 176), $a=b=9.6466(8)$, $c=7.1136(6)$ Å, $Z=1$) was synthesised in a potassium fluoride flux. The chemical composition was proven by EPMA/EDX and the structure refined from X-ray single crystal diffraction data ($R1(F^2>2\sigma(F^2))=0.0204$). The compound crystallises in the regular apatite structure. Potassium fills one (4*f*) out of two metal positions present in the structure with an occupancy factor of 25%. The remaining places of this site (Pr2/K2) are occupied by praseodymium. Oxygens of the silicate groups form a coordination polyhedron (CN=9) in the shape of a distorted threefold capped trigonal prism. These face sharing [(Pr2/K2)O_9]-polyhedra build up chains, which are inter-connected via SiO_4-groups. The resulting channel framework accommodates sevenfold oxygen-coordinated praseodymium (Pr1), attached to the inside of the tubes that are aligned parallel to the *c*-axis. The oxide ions O4, located on the longitudinal axis of the channels, exhibit anomalously high atomic displacement parameters along the *c*-direction. It can be shown that this property is in agreement with literature structural data as well as oxide ion conductivity of similar rare earth apatites.

Keywords: Apatite; Crystal growth; X-ray diffraction; Crystal structure

1. Introduction

The development of new hydrides based on titanium doped alanates moved the reversible hydrogen storage at low pressures and temperatures slightly above 100 °C to the realm of possibility [1]. In combination with oxide ion conductors working at moderate temperatures it could lead to intermediate temperature solid oxide fuel cells with excellent environmental compatibility, as the waste gas is pure water. This intensified the search for low-temperature oxide ion conducting materials, as the widely used yttria stabilised zirconia needs to be heated to 500 °C for operating [2]. The researches were stimulated by Nakayama et al. who introduced silicious rare earth (RE) oxyapatites as oxide ion conductors (review [3] and references therein). At the same time they were the only one so far who carried out anisotropic electric conductivity measurements on single crystals of this compound type: $RE_{9.33}(SiO_4)_6O_2$ (RE=Pr,Nd,Sm) [4,5] and $Nd_8Sr_2(SiO_4)_6O_2$ [6]. These measurements revealed an increasing anisotropic oxide ion conductivity in the series Sm<Nd<Pr that is most strongly pronounced for $Pr_{9.33}(SiO_4)_6O_2$. For this phase the conductivity is about two orders of magnitude larger parallel to the *c*-axis than in the perpendicular directions at 100 °C. Even more important is the fact that at 200 °C, the ionic conductivity along the *c*-axis surpasses that of the orthorhombic distorted perovskite $BaCe_{0.8}Gd_{0.2}O_3$ [7], a material for oxygen sensors that exhibits response properties enough for practical use even at 300 °C, by a factor of five. In contrast, $Nd_8Sr_2(SiO_4)_6O_2$ shows a large decrease of the ionic conductivity compared to $Nd_{9.33}(SiO_4)_6O_2$. In order to get a better understanding of this transport property we were encouraged to undertake a single crystal analysis of $Pr_{9.33}(SiO_4)_6O_2$ since no structural data on praseodymium oxyapatites were presented so far (except for an indexed powder pattern of the latter compound, Powder Diffraction File 23-1389 [8]). We tried to synthesise the

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phase in a potassium fluoride flux. Instead the title compound was obtained.

2. Experimental

2.1. Sample preparation and instrumentation

According to the theoretic reaction equation $4.67\ Pr_2O_3 + 6SiO_2 \xrightarrow{T} Pr_{9.33}(SiO_4)_6O_2$, 0.392 g Pr_2O_3 (1.189 mmol, Fluka, puriss.) and 0.095 g quartz (1.581 mmol, Fluka, purum) was placed in a platinum crucible and 0.85 g KF (14.6 mmol, Merck, p.A.) added as flux melting agent. The mixture was heated up to 1000 °C in 4 h and was kept at this temperature for 2 h. The temperature was then decreased to 800 °C within two days followed by cooling down to room temperature during 12 h. The solidified melt was leached with deionised water to remove the potassium fluoride and water soluble by-products. From the residue light-green hexagonal rods could be isolated for single crystal structure analysis.

The X-ray powder pattern was recorded on a Philips X'Pert diffractometer (λ = Cu–K$\alpha_{1,2}$ radiation), single crystal data were collected on a Siemens SMART diffractometer equipped with a CCD detector. EPMA/EDX was accomplished with a JEOL 6400 scanning electron microscope.

Table 1
Crystallographic data for $Pr_9K(SiO_4)_6O_2$

Crystal data	
Empirical formula	$Pr_9K(SiO_4)_6O_2$
CSD no.	415040
M [g/mol]	1891.83
Crystal system	Hexagonal
Space group	$P6_3/m$ (No.176)
Lattice parameters[a] [Å] $a=b$	9.6466(8)
c	7.1136(6)
V [Å^3]	573.28(8)
Formula units Z	1
X-ray density D_x [g/cm^3]	5.480
Crystal description	light green, transparent, hexagonal rod, 0.13 × 0.05 × 0.05 mm
Data collection	
Diffractometer/Wavelength/ Temperature [°C]	Siemens SMART/Mo–K$\bar{\alpha}$/20(2)
Absorption correction	SADABS [10]
Measured reflections	4480
Independent reflections all/$I>2\sigma(I)$	622/591
R_{int}	0.027
Structure solution and refinement	
Program for structure solution/refinement	SHELX [11]
Number of refined parameters	40
$R1(F^2>2\sigma(F^2))$	0.0204
$wR2$(all)	0.0491
S	1.255
Residual electron density $\Delta\rho_{max}/\Delta\rho_{min}$ [e/Å^3]	1.40 (0.74 Å from Pr1) / −1.02 (1.18 Å from O3)

[a] Lattice parameters of $Pr_{9.33}(SiO_4)_6O_2$ (calculated from the d-spacings given in [8]): $a=b=9.6096(3)$, $c=7.0695(1)$ Å, $V=565.37(5)$ Å^3.

Table 2
Standardised [12] atomic coordinates and equivalent displacement parameters [Å^2] for $Pr_9K(SiO_4)_6O_2$

Atom	Wyckoff position	x	y	z	U_{eq}
Pr1	6*h*	0.24684(4)	0.23603(4)	1/4	0.0112(1)
Pr2/K2[a]	4*f*	1/3	2/3	0.00118(8)	0.0128(2)
Si	6*h*	0.0271(2)	0.3981(2)	1/4	0.0086(3)
O1	12*i*	0.0884(5)	0.3404(6)	0.0690(6)	0.031(1)
O2	6*h*	0.1171(5)	0.5914(6)	1/4	0.019(1)
O3	6*h*	0.4823(6)	0.1660(6)	1/4	0.025(1)
O4	2*a*	0	0	1/4	0.102(9)

[a] Position mixed occupied: SOF Pr=0.75, SOF K=0.25.

The resulting fluorescence spectra were interpreted with the Genesis (EDAX) program.

2.2. Structure refinement

The space group could be unambiguously assigned to $P6_3/m$ .The starting structural model was obtained by direct methods. Since the cell parameters of the single crystal were clearly larger than those of $Pr_{9.33}(SiO_4)_6O_2$ (see footnote a in Table 1) it was deduced that potassium had been incorporated into the cation vacancies. In analogy to $Y_9Na(SiO_4)_6O_2$ [9] the 4*f* position was populated with 75% Pr and 25% K. As potassium could also go in the 6*h* position the occupancy factors of Pr and K on both sites (each constrained to a total occupation of 100%) were successively allowed to vary. The refinement gave almost unchanged populations whereby the potassium exclusively occupied the 4*f* position (26%) yielding a theoretical composition of "$Pr_{8.96(1)}K_{1.04(1)}(SiO_4)_6O_2$". This is in very good agreement with the stoichiometry of the starting model. Due to charge balance the K/Pr ratio on the 4*f* position was altered to the fixed value of 25/75% in the last refinement stage, which had no significant effect on the *R*-values. The crystallographic data and atom parameters are summarised in Tables 1, 2 and 3. The anomalously high anisotropic displacement parameter of the O4 atom parallel to the *c*-axis, U_{33} that could not be improved by a split model is discussed below. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-415040. To verify the composition EPMA/EDX was carried

Table 3
Anisotropic displacement parameters [Å^2] for $Pr_9K(SiO_4)_6O_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pr1	0.0090(2)	0.0124(2)	0.0103(2)	0	0	0.0039(1)
Pr2/K2[a]	0.0132(2)	0.0132(2)	0.0120(3)	0	0	0.00659(9)
Si	0.0076(7)	0.0069(7)	0.0094(7)	0	0	0.0022(5)
O1	0.033(2)	0.060(3)	0.018(2)	0.024(2)	0.014(2)	0.037(2)
O2	0.012(2)	0.021(2)	0.027(3)	0	0	0.010(2)
O3	0.022(2)	0.008(2)	0.030(3)	0	0	−0.004(2)
O4	0.016(3)	0.016(3)	0.27(3)	0	0	0.008(1)

[a] Position mixed occupied: SOF Pr=0.75, SOF K=0.25.