TU Clausthal

Synthesis and Crystal Structure of $SrH_2P_2O_6 \cdot 2\ H_2O$

Introduction

The alkaline-earth metal hypodiphosphates were first reported by Salzer [1]. The crystal structure of hypodiphosphates of alkaline-earth cations are unknown. In our investigations of the chemical behaviour of the alkali and alkaline earth hypodiphosphates, we have synthesized and structurally characterized the strontium dihydrogen hypodiphosphate dihydrate, $SrH_2P_2O_6 \cdot 2\ H_2O$.

The compound crystallizes in the monoclinic space group *C*2/*c* with *a* = 10.830(4), *b* = 6.268(1), *c* = 10.613(3) Å, *β* = 106.93(3) , *V* = 689.3(2) Å^3 and *Z* = 4.

Experimental

The new hypodiphosphate(IV) hydrate, $SrH_2P_2O_6 \cdot 2\ H_2O$, was synthesized by soft chemistry reaction from aqueous solution of $H_4P_2O_6 \cdot 2\ H_2O$ and strontium carbonate at 40 C. The solution was placed in a vacuum desiccator at 60 C. After some days standing at this constant temperature colourless plate–shaped crystals of the title compound were obtained from the solution.

The structure was verified by X-ray structure analysis and the Raman spectrum of the title compound was recorded and interpreted.

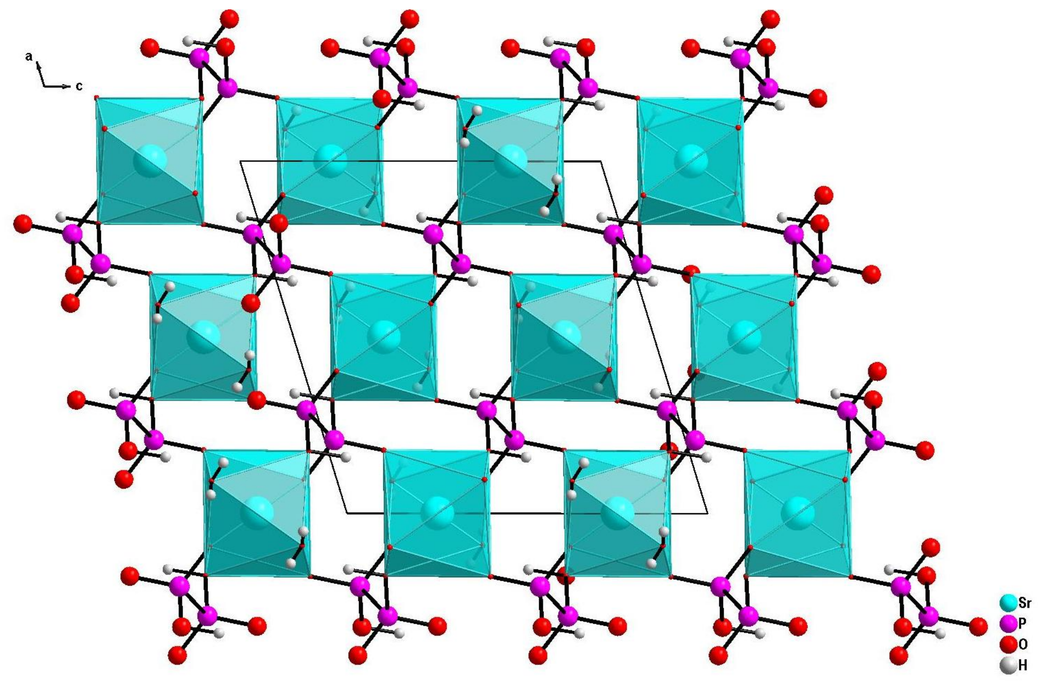

Fig. 1 Projection of the crystal structure of $SrH_2P_2O_6 \cdot 2\ H_2O$ along *b* axis.

Tab. 1 Crystallographic data and structure refinement parameter for $SrH_2P_2O_6 \cdot 2\ H_2O$.

Crystal system	monoclinic
Space group	*C*2/*c* (No. 15)
a [Å]	10.830(4)
b [Å]	6.268(1)
c [Å]	10.613(3)
β [ ]	106.93(3)
Volume [Å^3]	689.3(3)
Z	4
D_{calc} [g · cm^{-3}]	2.733
Temperature [K]	223(2)
μ (Mo-K_α) [mm^{-1}]	8.289
Θ range [°]	1.00 – 25.34
F(000)	552
h_{min}, h_{max}, k_{min}, k_{max}, l_{min}, l_{max}	-12, 12, -7, 7, -12, 12
Reflections collected	5197
Unique reflections	634
Data / refined parameters	634 / 64
Goodness-of-Fit	1.081
*R*1 [*I*>2σ(*I*)]	0.0339
*wR*2 [*I*>2σ(*I*)]	0.0687
*R*1(all data)	0.0436
*wR*2 (all data)	0.0718
Largest res. Peak [e Å^3]	0.820 / -0.737

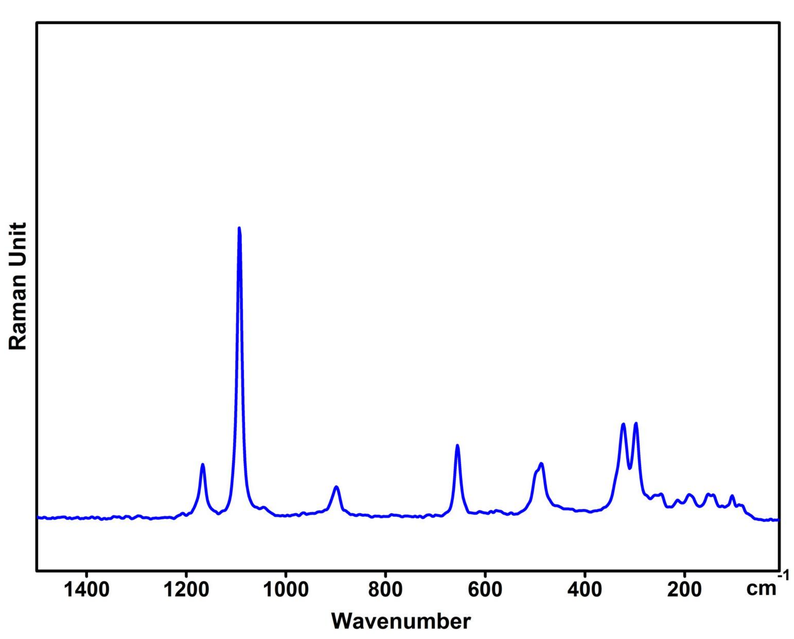

Fig. 4 FT-Raman spektrum ($\lambda_{exc.}$=1064 nm) of crystalline $SrH_2P_2O_6 \cdot 2\ H_2O$ (Raman intensity in arbitrary units).

Structure description

The crystal structure of the title compound is characterized by discrete $[H_2P_2O_6]^{2-}$ anions in staggered conformation, $[SrO_8]$ polyhedra and water molecules, held together by hydrogen bonds (Fig. 1 and Tab. 1). The Sr^{2+} cations are eightfold coordinated by O atoms of six anions and two water molecules. The distances between the strontium and the oxygen atoms range between 2.533 and 2.809 Å (Tab. 2), and are thus comparable to those in related compounds, as e. g. $Sr_2P_2S_6 \cdot 10\ H_2O$ [2]. The coordination polyhedron of Sr^{2+} might be considered as a distorted bicapped trigonal prism (by O(1) and O(4), $CN_{(Rb)}$ = 8) (Fig. 2). The water molecules are included in the coordination sphere of Sr^{2+} cation. The main characteristic of the $SrH_2P_2O_6 \cdot 2\ H_2O$ structure is the $[H_2P_2O_6]^{2-}$ anion. The discrete ethane-like $[H_2P_2O_6]^{2-}$ anions in staggered conformation are on a center of inversion with P - P distances of 2.167 Å. The P - P central bond links two PO_3 groups with P - O distances from 1.511 to 1.588 Å. As expected, in $SrH_2P_2O_6 \cdot 2\ H_2O$, the bond distances and angles of the $[H_2P_2O_6]^{2-}$ anions are similar of those in $Na_2H_2P_2O_6 \cdot 6\ H_2O$ and $(NH_4)_2H_2P_2O_6$ [3, 4].

The hydrogen-bond lengths between O atoms of water molecules and O atoms of $[P_2O_6]^{4-}$ range from 2.644 to 2.802 Å, the O – H ··· O angles from 161.2 to 176.9 (Tab. 2 and Fig. 3). These values agree very well with those reported previously [5, 6].

The FT-Raman spectrum is presented in Fig. 4. The spectral region below 650 cm^{-1} belongs to $[H_2P_2O_6]^{2-}$, in which the characteristic P – O and P – P stretchings and bendings can be recognized besides the lattice vibrations below about 150 cm^{-1}.

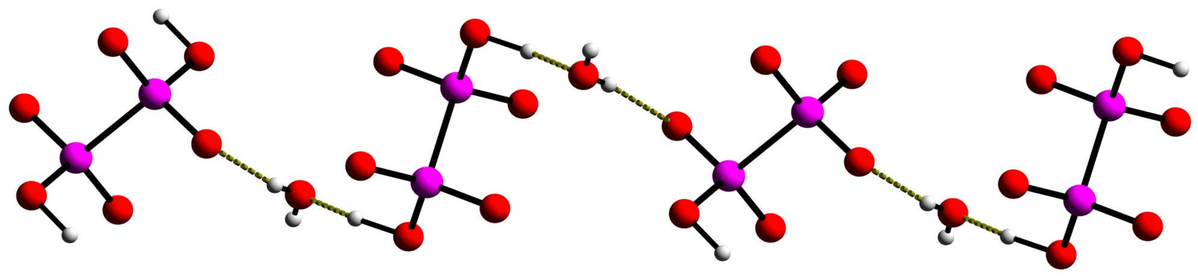

Fig. 3 The hydrogen-bonds in the crystal structure of $SrH_2P_2O_6 \cdot 2\ H_2O$.

Tab. 2 Selected distances [Å] and angles [ ] for the title compound.

$[H_2P_2O_6]^{2-}$ ion			
P – P^{i}	2.167(3)	O1 – P – O2	117.4(2)
P – O1	1.511(3)	O1 – P – O3	111.9(2)
P – O2	1.515(3)	O2 – P – O3	107.8(2)
P – O3	1.588(3)	O1 – P – P	110.9(2)
H – O2	0.721(4)	O2 – P – P	108.0(2)
Sr^{2+} coordination			
Sr – O2	2.533(3)	Sr – O3	2.620(3)
Sr – O2^{i}	2.533(3)	Sr – O3^{iii}	2.620(3)
Sr – O1	2.570(3)	Sr – O4	2.809(3)
Sr – O1^{ii}	2.570(3)	Sr – O3^{iv}	2.809(3)
Hydrogen bonds			
O3 – H3 – O3^{ii}	2.644(1)	∠ O3 – H3 – O3^{ii}	176.9(5)
O4 – Hb – O3	2.745(2)	∠ O4 – Hb – O3	161.2(5)
O4 – Ha – O3^{ii}	2.802(1)	∠ O4 – Ha – O3^{ii}	158.8(5)

i) –x+1, -y+1, -z+1; ii) x, -y+1, z-1/5; iii) –x+1, y, -z+1/2, iv) x, -y, z+1/2.

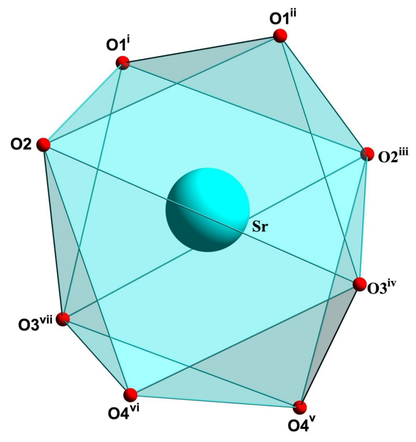

Fig. 2 Sr coordination in $SrH_2P_2O_6 \cdot 2\ H_2O$.

References

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