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Synthesis and characterization of alkali-metal tin(II) phosphates: $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ and $K_2SnP_2O_7$

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Abstract

Two new alkali-metal tin(II) phosphates – $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (**1**) and $K_2SnP_2O_7$ (**2**) – were synthesized by high-temperature reactions and structurally characterized by single-crystal X-ray diffraction. $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ crystallized in the noncentrosymmetric space group $P\text{-}62c$ (No. 190) with $a = 9.6445(1)$ Å, $b = 9.6445(1)$ Å, $c = 34.059(6)$ Å, $V = 2743.6(7)$ Å^3 and $Z = 1$. $K_2SnP_2O_7$ crystallized in the monoclinic space group $P2_1/n$ with $a = 9.856(3)$ Å, $b = 6.7244(1)$ Å, $c = 12.225(3)$ Å, $\beta = 108.240(5)^\circ$, $V = 769.5(3)$ Å^3 and $Z = 4$. Both structures exhibit a novel open-framework structure. The crystal structure of **1** contains SnO_3 and SnO_4 polyhedra sharing corners with $[HPO_4]^{2-}$, $[PO_4]^{3-}$ and $[P_2O_7]^{4-}$ groups, which form tunnels of six rings filled with Na^+ cations and parallel to the c-axis, which are connected via O–Sn–O bridges to form a three-dimensional open framework. The crystal structure of **2** contains SnO_4 seesaw polyhedra sharing corners with diphosphate groups to form a three-dimensional $[SnP_2O_7]^{2-}$ framework that exhibits a tunnel structure of 10- and 12-membered rings expanding along [011] and [100] with four arrays of K^+ cations located in channels of the framework.

Keywords: Tin(II) phosphate; Crystal structure; Noncentrosymmetric; Channel structure

1. Introduction

Metal phosphates exhibit varied structural types that have been the subject of intensive research [1–4]. Much attention has been devoted to the synthesis of open-framework metal phosphates, which might produce large void volumes for prospective applications such as chemical sensors and receptors for selective catalysis [5]. Many main-group metals, such as group III (Al, Ga, In), IV (Ge, Sn, Pb), and V (As–Sb–Bi) can cooperate with phosphate units to form open-framework structures [1]. Among these compounds, tin phosphates are rare compared to other phosphate compounds [1]. Several authors have shown that tin(II) phosphates are interesting inorganic materials for lithium-ion battery and catalysts [5–8]. The Sn^{2+} cation contains nonbonded 5s electron pairs, which tend to coordinate with ligands in an acentric environment. Tin phosphates have thus become appealing in this regard as they offer interesting open-framework structures with possible noncentrosymmetric crystal structures showing a nonlinear optic property. Many tin phosphates have been structurally characterized [9–22]. Despite many efforts that show hydrothermal synthesis to be the most effective synthetic route to prepare open-framework tin(II) phosphates [23–36], the solid-state method tends to form a robust structure, which makes the compound capable of undertaking ion exchange and a large ionic conductivity. Our group has demonstrated that A_2HPO_4 and metal can serve as reducing and oxidizing reagents to synthesize metal phosphates, and several known compounds, such as $A_2MP_2O_7$ (A = Na, K; M = Pb, Zn) and $KZnBP_2O_8$, have been successfully synthesized [37–39]. We extended this research to the tin phosphate system and two new tin phosphates with unprecedented structural types were synthesized. As confirmed by measurements on single crystals, the synthesis of $K_2SnP_2O_7$ is presented as follows:

$$4K_2HPO_4 + 3Sn + SnO_2 + 2P_2O_5 \rightarrow 4K_2SnP_2O_7 + 2H_2$$

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In a reaction in which Na replaced K, a new phase $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ was synthesized.

The compounds described here, with a channel structure, are interesting examples of tin phosphates prepared according to the solid-state synthetic route. Here we report the synthesis, structure and characterization of two new tin phosphates.

2. Experiments

2.1. Synthesis

$Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (**1**) and $2K_2SnP_2O_7$ (**2**) were synthesized by solid-state methods. The starting reagents were A_2HPO_4 (A = Na, K, 99.999%, Sigma), Sn (99.9%, Alfa), SnO_2 (99.9%, Sigma) and P_2O_5 (99.999%, J.T. Baker). In a typical reaction, precursors in stoichiometric proportions were mixed in an Ar-filled glove box (total mass ~ 0.5 g), placed in a silica tube, sealed under vacuum ($P \sim 10^{-4}$ torr), and heated slowly to 600 °C over 48 h, followed by cooling in the furnace to 22 °C on switching off the power. To avoid a possible explosion due to the formation of gaseous hydrogen, the length of reaction tube was kept about 7–8 cm (id = 0.9 cm). The products contain colorless and transparent crystals, rod- and plate-shaped for **1** and **2**, respectively. According to powder X-ray diffraction, the synthesis of **1** has a byproduct $Na_5P_3O_{10}$, and the reaction of **2** yields an impure KPO_3. Attempts to synthesize analogues using K^+ in **1** and Na^+ in **2** failed.

2.2. Single-crystal X-ray diffraction

Single crystals of compounds **1** ($0.3 \times 0.4 \times 0.85$ mm^3) and **2** ($1.3 \times 0.25 \times 0.2$ mm^3) were mounted on glass fibers with epoxy glue; intensity data were collected on a diffractometer (Bruker APEX CCD) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The distance from crystal to detector was 5.038 cm. Data were collected with a scan 0.3° in groups of 600 frames each at ϕ settings 0° and 60°. The duration of exposure was 30 and 20 s/frame for **1** and **2**, respectively. The 2θ values varied between 2.40° and 56.48°. Diffraction peaks obtained from all frames of reciprocal space images were used to determine the unit-cell parameters. The data were integrated using the Siemens SAINT program and were corrected for Lorentz and polarization effects [40]. Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements of numerous reflections. The structural model was obtained by direct methods and refined by full-matrix least-square refinement based on F^2 using the SHELXTL package [41]. The rod-shaped crystal of **1** revealed a hexagonal unit cell ($a = 9.6445(1)$ Å, $c = 34.059(6)$ Å, $V = 2743.6(7)$ Å^3) and the systematic absence conditions were consistent with space groups *P*-31*c* (No. 163), *P*31*c* (No. 159), *P*6$_3$*mc* (No. 186), *P*6$_3$/*mmc* (No. 194), and *P*-62*c* (No. 190). An initial model of the crystal structure was built in the centrosymmetric space groups. However, the diffraction data refinements indicate that the structure was not centrosymmetric and the noncentrosymmetric space group *P*-62*c* (No. 190) was found to be correct during structure refinement. The hydrogen atoms for **1** were observed with difference Fourier maps. Atomic positions were refined with anisotropic displacement parameters except O5 and O11 sites; fixed isotropic displacement parameters 0.02 was applied for H atom. Final structural refinements produced $R1/wR2 = 0.039/0.0886$. The plate-shaped crystal of **2** revealed a monoclinic unit cell ($a = 9.856(3)$ Å, $b = 6.7244(1)$ Å, $c = 12.225(3)$ Å, $V = 769.5(3)$ Å^3); systematic absences indicated space group $P2_1/n$ (No. 14). Final structural refinements produced $R1/wR2 = 0.0170/0.0431$. Crystallographic data and selected bond distances for **1** and **2** are given in Tables 1–3. Further details of the crystal-structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-419265 for $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)12$ (**1**) and CSD-419264 for $K_2SnP_2O_7$ (**2**).

2.3. Characterizations

X-ray powder diffraction data of the products were measured at 22 °C on a powder diffractometer (Bruker D8 Advance Bragg–Brentano-type, operated at 40 kV and 40 mA; Cu Kα, $\lambda = 0.15418$ nm). For phase identification, XRD data were collected in a 2θ range from 5° to 70° with a step interval 0.02°. Infrared spectra were recorded on a spectrometer (BIO-RAD FTS 165 FT-IR) in the range 400–4000 cm^{-1}, with the sample pressed between two KBr pellets. Differential scanning calorimetry (DSC) was performed with a thermal analyzer (Setaram Labsys DSC131). A powder sample (approximately 20 mg) was placed in an alumina crucible and Al_2O_3 powder served as a reference sample. The sample was heated to 800 °C at 5 °C min^{-1} under flowing N_2.

3. Results and discussion

3.1. Structure of $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$

Analysis of single-crystal X-ray diffraction data for **1** initially revealed 11 unique sites for Na, Sn and P and 11 unique sites for O atoms. The charge balance of the structure dictates that six further hydrogen cations must be found in one asymmetric unit, which were observed with a differential Fourier map; they were located in crystallographic general positions close to O11, giving a formulation of six $[HPO_4]^{2-}$ for the asymmetric unit. The structural analysis yielded a charge-balanced formula $Na^+_{10}Sn^{2+}_{31}(HPO_4)^{2-}_6(P_2O_7)^{4-}_6(PO_4)^{3-}_{12}$. The structure of **1** consists of $[HPO_4]^{2-}$, $[PO_4]^{3-}$ and $[P_2O_7]^{4-}$ layers stacked along the *c*-axis with a repeat sequence of four layers $[HPO_4]^{2-}$–$[PO_4]^{3-}$–$[P_2O_7]^{4-}$–$[PO_4]^{3-}$, which are connected to each other by Sn(II) atoms to form a three-dimensional framework. The structure contains channels running along the [001] direction with Na cations located in

Table 1
Crystallographic data for $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ and $K_2SnP_2O_7$

Formula	$Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$	$K_2SnP_2O_7$
Crystal size/mm^3	$0.3 \times 0.17 \times 0.13$	$0.43 \times 0.13 \times 0.1$
Formula mass/g mol^{-1}	6668.44	370.83
Temperature/K	298(2)	298(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Hexagonal	Monoclinic
Space group	*P*-62*c* (No. 190)	$P2_1/n$ (No. 14)
a/Å	9.6445(1)	9.856(3)
b/Å		6.7244(1)
c/Å	34.059(6)	12.225(3)
β		108.240(5)
V/Å^3	2743.6(7)	769.5(3)
Z	1	4
Density/g cm^{-3}	4.036	3.202
Absorption coeff/mm^{-1}	7.530	3.609
Transmission range	0.826525−1	0.814413−1
Independent reflections	2310 [R(int) = 0.0336]	1888 [R(int) = 0.0171]
GOF on F^2	1.149	1.066
$R1/wR2$ [$I > 2\sigma(I)$]	0.039/0.0886	0.0170/0.0431
$\Delta\rho$ (e/Å^3)	2.365 and −1.273	0.492 and −0.421

Table 2
Atomic positional coordinates, isotropic displacement parameters (Å$^2 \times 10^3$), and site occupancies

$Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (**1**)						
Atoms	Site	*x*	*y*	*z*	*U* (eq)	Occ.
Sn1	12i	0.0800(1)	0.6722(1)	0.1558(1)	30(1)	
Sn2	12i	0.5926(1)	0.6834(1)	0.0544(1)	14(1)	
Sn3	4f	0.6667	0.3333	0.1963(1)	17(1)	0.545(5)
Sn4	6h	0.6035(2)	0.6894(2)	0.25	31(1)	0.592(4)
Sn5	4f	0.6667	0.3333	0.0996(1)	32(2)	0.282(5)
P1	6h	0.3414(3)	0.2698(2)	0.0392(1)	11(1)	
P2	12i	0.9547(5)	0.6564(5)	0.25	27(1)	
P3	12i	0.7435(3)	0.6828(3)	0.1487(1)	13(1)	
Na1	4e	0	0	0.2033(2)	26(1)	
Na2	4e	0	0	0.0954(2)	23(1)	
Na3	2a	0	0	0	13(2)	
O1	12i	0.7220(8)	0.7365(8)	0.1080(2)	27(1)	
O2	12i	0.9241(9)	0.762(1)	0.1561(2)	50(3)	
O3	6h	0.7895(7)	0.9539(7)	0.0482(2)	13(1)	
O4	12i	0.763(6)	0.6347(7)	0.0274(2)	16(1)	
O5	12i	0.838(1)	0.337(1)	0.1515(2)	40(2)	
O6	12i	0.038(1)	0.836(1)	0.25	31(2)	
O7	6g	0.3793(8)	0.3793(8)	0	11(1)	
O8	12i	0.4614(8)	0.3801(8)	0.0691(2)	23(1)	
O9	12i	0.003(1)	0.5961(9)	0.2140(2)	47(2)	
O10	12i	0.6719(8)	0.7488(7)	0.1793(2)	19(1)	
O11	6h	0.770(3)	0.585(2)	0.25	91(6)	
$K_2SnP_2O_7$ (**2**)						
Atoms	Site	*x*	*y*	*z*	*U* (eq)/Å	
Sn1	4e	0.2527(1)	0.1614(1)	0.5046(1)	15(1)	
K1	4e	0.8199(1)	0.8551(1)	0.8429(1)	23(1)	
K2	4e	0.3660(1)	0.1274(1)	0.8529(1)	21(1)	
P1	4e	0.0106(1)	0.1309(1)	0.6489(1)	12(1)	
P2	4e	0.5073(1)	0.1388(1)	0.3553(1)	12(1)	
O(1)	4e	0.1402(2)	0.0242(2)	0.6348(1)	23(1)	
O(2)	4e	0.8887(1)	0.9834(2)	0.6428(1)	22(1)	
O(3)	4e	0.6351(1)	0.1131(2)	0.4658(1)	21(1)	
O(4)	4e	0.5372(2)	0.8095(2)	0.9242(1)	25(1)	
O(5)	4e	0.8838(2)	0.2566(2)	0.8797(1)	26(1)	
O(6)	4e	0.0684(1)	0.2002(2)	0.7832(1)	19(1)	
O(7)	4e	0.4694(2)	0.9504(2)	0.2892(1)	26(1)	

channels of the framework as shown in Fig. 1. Each channel is made up of six-membered ring units constructed with alternate corner-shared [PO_4] and SnO_3 (or SnO_4) units, which are additionally stacked along the *c*-axis via O−M−O bridges (M = Sn, P) of the phosphate groups and Sn atoms. The six-ring window is distorted with three O atoms pointing inside the channel so as to decrease the size of the channel. These hexagonally arrayed six-ring channels are connected by interstitial SnO_3 pyramids to construct the three-dimensional framework. The atomic sites for tin atoms contain two fully occupied and three partially occupied positions. Each Sn^{2+} cation is asymmetrically coordinated to three or four oxygen

Table 3
Selected interatomic distances (Å) for **1** and **2**

$Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$			
Sn1−O2	2.08(1)	P1−O3	1.536(6)
Sn1−O9	2.116(6)	P1−O4	1.546(6)
Sn1−O10	2.287(6)	P1−O7	1.626(4)
		P1−O8	1.509(7)
Sn2−O1	2.123(6)		
Sn2−O3	2.346(6)	P2−O6	1.505(7)
Sn2−O4	2.131(5)	P2−O9	1.527(6)(×2)
Sn3−O5	2.237(8)(×3)	P2−O11	1.56(2)
Sn4−O6	2.35(1)	P3−O1	1.531(6)
Sn4−O10	2.486(6)(×2)	P3−O2	1.533(8)
Sn4−O11	2.28(2)	P3−O5	1.521(9)
		P3−O10	1.552(6)
Sn5−O5	2.411(9)(×3)		
Sn5−O8	2.469(6)(×3)		
$K_2SnP_2O_7$			
Sn1−O1	2.3909(2)	P2−O3	1.5416(1)
Sn1−O2	2.1371(1)	P2−O5	1.5142(2)
Sn1−O3	2.1235(1)	P2−O6	1.6267(1)
Sn1−O5	2.3539(2)	P2−O7	1.4859(2)
P1−O1	1.5209(2)		
P1−O2	1.5418(1)		
P1−O4	1.4825(2)		
P1−O6	1.6283(1)		

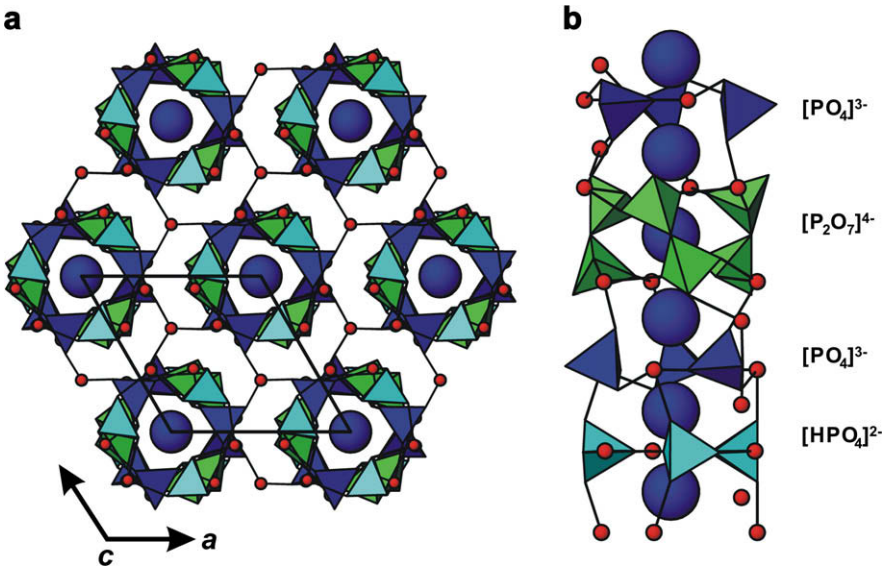

Fig. 1. (a) Polyhedral representation of **1** viewed along the crystallographic *c*-axis [001] showing six-membered ring windows. The big blue and small red circles denote Na^+ and Sn^{2+} atoms, respectively. (b) The six-membered channel along the Na^+ showing a stacking sequence of HPO_4 (light blue), PO_4 (blue) and P_2O_7 (green) polyhedra. H atoms are omitted for clarity.

atoms due to the lone-pair electrons. The Sn1, Sn2 and Sn3 (54% Sn) sites in the asymmetric unit exhibit a distorted trigonal-pyramid coordination, with three shorter Sn–O distances (2.08(1)–2.346(6) Å). The Sn4 (59% Sn) atom in the asymmetric unit exhibits a distorted seesaw-shaped coordination, with two shorter Sn–O distances (2.28(2) and 2.35(1) Å) and two longer distances (2.486(6) ×2 Å). The Sn5 (28% Sn) sites are located between the six-ring channels, and the coordination polyhedra around these sites are distorted octahedra with Sn–O distances 2.411(9) (×3) and 2.469(6) Å (×3). The observed Sn–O bond lengths (2.08(2)–2.486(6) Å) are within the normal range of similar tin phosphate compounds. Three crystallographically independent phosphorus atoms exist in the structure, all tetrahedrally coordinated with P–O distances in a range 1.507(1)–1.626(4) Å. The diphosphate group is in a nearly eclipsed conformation. The $[HPO_4]^{2-}$ unit contains the P–OH group as shown by the longer P–O distances 1.56(2) Å (P(2)–O(11)). The channel with diameter approximately 2.7 Å encapsulates an array of Na^+ cations coordinated by nine (Na1, Na2) or six (Na3) oxygen atoms with Na–O distance 2.392(9)–2.980(7) Å. The six-ring window of **1** is also found in a tin phosphate compound $NaSn_4P_3O_{12}$ [36], but that compound presented no channel structure. The bond valence sum calculations carried out on the fully occupied positions indicate that the individual bond valencies of Na, Sn, P, and O are 1+, 2+, 5+, and 2−, respectively [42]. For partially and mixed occupied positions (Sn3–Sn4), the bond valence sum values for Sn are in the range of 1.62–1.80, indicative of partially occupied sites.

3.2. Structure of $K_2SnP_2O_7$

The structure of **2** differs considerably from compounds with general formula $A_2PbP_2O_7$ (A = Na, K) [37,38], although they share the same general formula. The compound contains a three-dimensional $[SnP_2O_7]^{2-}$ framework with K cations located in channels of the framework as shown in Fig. 2. X-ray measurements on a single crystal reveal five unique sites for K, Sn and P and seven unique sites for O atoms. The crystal structure consists of SnO_4 seesaw polyhedra sharing corners with $[P_2O_7]^{4-}$ diphosphate groups. There are two crystallographically independent potassium atoms in the structure, each of which is coordinated by nine or seven O atoms with K–O distances 2.624 (4)–3.392 (4) Å. Each Sn^{2+} cation is bonded to four oxygen atoms in asymmetric coordination environments (seesaw shaped) due to its lone pair. The observed Sn–O bond lengths, 2.124(4)–2.389(4) Å, are within the normal range compared to similar tin phosphate compounds. The P ions are at the centers of regular coordination tetrahedra for each $[P_2O_7]^{4-}$ unit with a mean P–O distance 1.542 Å. The diphosphate group is in a nearly eclipsed conformation. The shortest P–O distance in each $[P_2O_7]^{4-}$ corresponds to the unshared oxygen atom. The structure of **2** is describable as being formed by layers of aligned $[P_2O_7]^{4-}$ units parallel to the *c*-axis, which are connected by asymmetric SnO_4 polyhedra along the *b*-axis to form a three-dimensional framework. Each $[P_2O_7]^{4-}$ unit shares four corners with four separate SnO_4; the unshared corners of diphosphate are directed into the channel containing the potassium ions. The connection between SnO_4 polyhedra and diphosphates produces large tunnels along the [100] and [011] directions. The channel along [100] contains puckered 12-membered rings (~4.4 × 8.2 Å) of corner-sharing $[P_2O_7]$ (×4) and SnO_4 (×4) polyhedra in a herringbone arrangement. The channel encapsulates four arrays of K atoms, which exhibit a nearly rectangular atomic packing. Although the channel is made of a 12-ring window, the ring is distorted with two O atoms pointing inside the channel so as to decrease

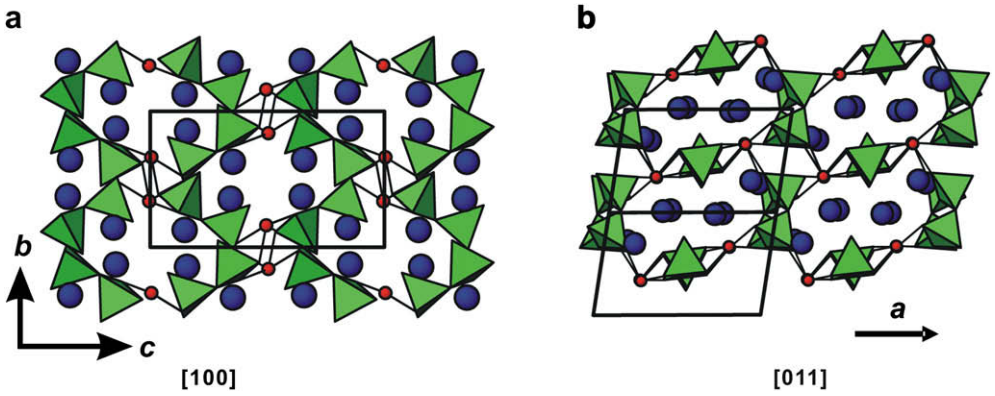

Fig. 2. (a) A [010] view of **2**. (b) and (c) 10- and 12-ring channels along [100] and [011] directions. The P_2O_7 units are indicated as green polyhedra and K^+ and Sn^{2+} atoms are shown as blue and red circles, respectively.

its size. The channel along [011] contains a 10-membered ring (~4.3 × 8.3 Å) built of corner-sharing $[P_2O_7]$ (×2), $[PO_4]$ (×2, from $[P_2O_7]^{4-}$) and Sn(II) atoms (×4), which are connected by sharing corners of P_2O_7 and SnO_4. The [011] channel contains four zigzag arrays of potassium atoms. The 12-ring channels parallel to [100] are intersected by 10-membered ring channels along the [011] and [01-1] directions to form a complex three-dimensional structure. The bond valence sum calculations carried out in the framework indicate that the individual bond valencies of K, Sn, P, and O are 1+, 2+, 5+, and 2−, respectively, which is in agreement with the charge-balanced model in $K_2^+Sn^{2+}(P_2O_7)^{4-}$ compound.

3.3. Characterizations

The IR spectrum of compound **1** exhibits a strong absorption at 3000 cm^{-1} and weak lines at 1293 and 1648 cm^{-1}, which are ascribed to the characteristic −OH vibration and the stretching vibration of HPO_4 groups (Fig. 3). The features between 940 and 1100 cm^{-1} are associated with symmetric and antisymmetric stretchings of P−O bonds in PO_4 group. Several low and middle absorption bands in the 670–800 cm^{-1} region are assigned to Sn−O bond vibrations. The existence of these IR absorptions supports the single-crystal structure in which the compound contains the HPO_4 group. The IR spectrum of **2** shows similar features as **1** that is associated with the asymmetric stretching vibrations of P−O and Sn−O units, respectively. There is no obvious absorption in a range near 3000 cm^{-1}, indicating the absence of an −OH group, consistent with its single-crystal structure. The DSC measurements obtained on heating the polycrystalline samples reveal distinct endothermic maxima at 626 and 716 °C for **1** and **2**, respectively, indicating melting points for each compound (Fig. 4). Powder X-ray experiments indicate that the residues contain SnO_2 and $ASn_4(PO_4)_3$ (A = Na, K).

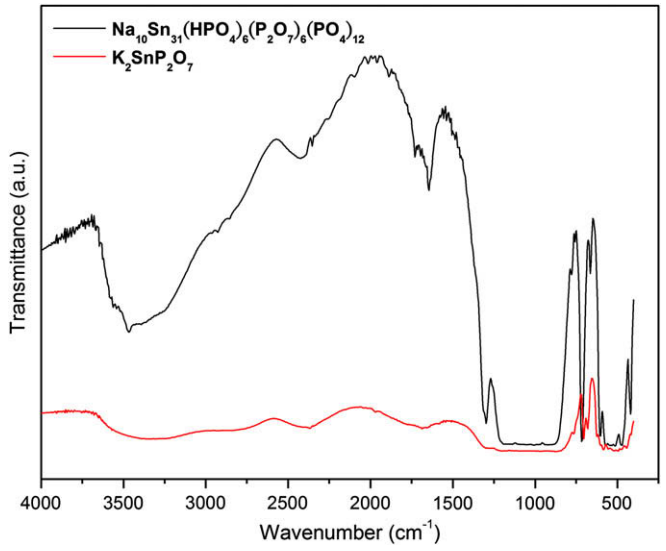

Fig. 3. IR spectra of $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (black) and $K_2SnP_2O_7$ (red).

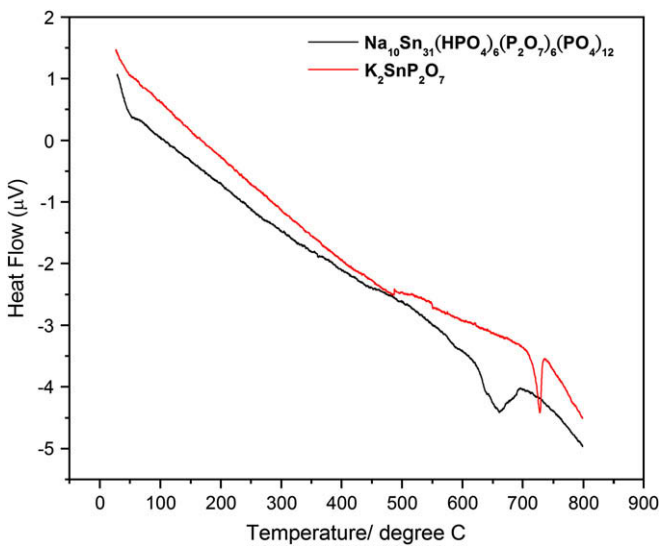

Fig. 4. DSC curves of $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (black) and $K_2SnP_2O_7$ (red).

4. Conclusion

We have synthesized two tin(II) phosphates that exhibit unique framework structures. Together with previous work on lead and other metals, these results on tin indicate that the reaction between A_2HPO_4 and metals or metal oxides can affect the synthesis of open-framework materials. We expect this method to be applicable to not only tin phosphates but also on choosing the corresponding reagents, other systems, such as boron, gallium, and indium phosphates, which might yield further exceptional open-framework structures.

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