

Hydrothermal Synthesis and Structural Characterization of a Novel Hydroxo Stannate: $\text{Sr}_2\text{Sn}(\text{OH})_8$

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A new hydroxo stannate(IV), $\text{Sr}_2\text{Sn}(\text{OH})_8$, has been synthesized by the hydrothermal method. Single-crystal X-ray diffraction shows that this compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.006(1) \text{ \AA}$, $b = 11.058(2) \text{ \AA}$, $c = 6.129(2) \text{ \AA}$, $\beta = 112.98(2)^\circ$, $V = 374.8(2) \text{ \AA}^3$, $Z = 2$, $R = 0.022$ ($I > 2\sigma(I)$). The structure $[\text{Sr}(\text{OH})_{6/3}(\text{OH})_{2/2}]_2[\text{Sn}(\text{OH})_{6/3}]$ consists of $\text{Sn}(\text{OH})_6$ octahedra and $\text{Sr}(\text{OH})_8$ triangulated dodecahedra. These $\text{Sr}(\text{OH})_8$ and $\text{Sn}(\text{OH})_6$ polyhedra form a novel complex 3D packing arrangement that contains channels running along $[001]$, filled with the in-pointing hydrogens of the hydroxo groups. © 2000 Academic Press

Key Words: structure; hydrothermal synthesis; extended framework; tin(IV).

INTRODUCTION

There has been much interest recently in the synthesis and characterization of new materials by soft chemistry approaches that provide effective routes for synthesizing new functional materials with new architectures. The hydrothermal method as such a soft route has been used to prepare a number of chemical stoichiometric complex oxides including MTiO_3 , MZrO_3 ($M = \text{Ca}, \text{Ba}, \text{Sr}, \text{or Pb}$) and their solid solutions (1). Results from both experimental and thermodynamic modeling demonstrate that hydrothermal synthesis of MO ($M = \text{Ca}, \text{Sr}, \text{Ba}, \text{or Pb}$) with TiO_2 and/or ZrO_2 under alkaline conditions usually leads to the formation of ABO_3 -type complex oxides with perovskite structure, such as SrTiO_3 , SrZrO_3 , and $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ (1). As far as we know, however, no studies have been reported on direct hydrothermal synthesis of MSnO_3 complex oxides at temperatures below 260°C . We are interested in these compounds because of their applications in materials technology as a constituent in perovskite solid solutions with ABO_3 -type complex oxides such as BaTiO_3 (2). Kutty

and Vivekanandan have attempted to prepare pure BaSnO_3 by a hydrothermal reaction starting from $\text{SnO}_2 \cdot \text{XH}_2\text{O}$ gel and $\text{Ba}(\text{OH})_2$ at $150\text{--}260^\circ\text{C}$, which invariably led to the formation of hydroxide phases (2). This suggests that the chemical properties of tin compounds under alkaline hydrothermal conditions are different from those of titanium and zirconium, although they all adopt similar six-coordination in aqueous solutions, oxides, hydroxides, and hydrates (3). Many hydrothermally synthesized 1-D, 2-D, and 3-D architectures are constructed by the SiO_4 , AlO_4 , and PO_4 tetrahedra (4) and/or based on four-, five- and/or six-coordinated metal species (5).

Here we report on the synthesis and characterization of a novel hydroxo stannate (IV), $\text{Sr}_2\text{Sn}(\text{OH})_8$, which we have discovered during the course of investigations on MO-SnO_2 systems with hydrothermal methods.

EXPERIMENTAL

All the reagents were commercially available, high-grade purity materials (Aldrich Chemicals, Shantou Guanghua Chemicals, Rugao Chemicals), used as supplied, without further purification. IR spectra with samples in KBr pellets were collected on a Perkin-Elmer PC-16 spectrometer. X-ray powder diffraction spectra were collected on a Philips PW1830 horizontal-scan diffractometer. Thermal analyses were performed in air on a Perkin-Elmer TGA 7 instrument with a heating rate of $5^\circ\text{C}/\text{min}$.

Hydrothermal Synthesis

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in distilled water and mixed thoroughly to form a homogeneous solution. NaOH solution was then added into the mixture under magnetic stirring and the mixture gradually became milk-like. The final mixture in the ratio of 2.2 SrCl_2 : 1.0 SnCl_4 : 20.0 NaOH : 350 H_2O was transferred into a stainless steel autoclave with a Teflon liner and heated to 230°C .

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TABLE 1
Crystal Data for Sr₂Sn(OH)₈

Formula	Sr ₂ Sn(OH) ₈	<i>M</i>	429.99
Crystal system	Monoclinic	Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> /Å	6.006(1)	<i>T</i> /Å	20
<i>b</i> /Å	11.058(2)	<i>λ</i> /Å	0.71073
<i>c</i> /Å	6.129(2)	<i>V</i> /Å ⁻³	374.8(2)
<i>β</i> /°	112.98(2)	<i>Z</i>	2
<i>D_c</i> /g cm ⁻³	3.811	<i>μ</i> /mm ⁻¹	174.91
<i>R</i> indices ^a [<i>F</i> _o > 4σ(<i>F</i> _o)] (837 data)	<i>R</i> ₁ 0.0222, <i>wR</i> ₂ ^b 0.0525		
<i>R</i> indices ^a (all data)	<i>R</i> ₁ 0.0250, <i>wR</i> ₂ ^b 0.0541		

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.
Weighting: $w^{-1} = \sigma^2(F_o^2) + (0.0347P)^2 + 0.0988P$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for Sr₂Sn(OH)₈

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Sn	0.0000	0.0000	0.0000	0.00617(11)
Sr	0.27400(6)	0.37022(3)	0.10456(6)	0.00870(11)
O(1)	0.0177(5)	0.1715(2)	-0.1275(5)	0.0108(5)
O(2)	-0.1183(5)	0.0603(2)	0.2527(5)	0.0098(5)
O(3)	0.3485(5)	0.0249(2)	0.2412(5)	0.0120(5)
O(4)	0.5516(5)	0.2269(2)	0.0214(5)	0.0147(6)
H(1)	-0.1224(5)	0.1819(2)	-0.2181(5)	0.013
H(2)	-0.2301(5)	0.1060(2)	0.1793(5)	0.012
H(3)	0.4086(5)	0.0814(2)	0.1967(5)	0.014
H(4)	0.6288(5)	0.2645(2)	-0.0407(5)	0.018

Note. *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

The reaction was maintained under autogeneous pressure for 1 week before being cooled naturally to room temperature. The resulting product, containing colorless elongated single crystals, was filtered and washed thoroughly with distilled water. Synthesis under a different molar ratio of NaOH within a wide range of 15.0–50.0 gave always the pure compound, as confirmed by X-ray powder diffraction.

Crystallography

A colorless, column-shaped crystal with dimensions of 0.160 × 0.064 × 0.032 mm was selected for single-crystal

X-ray crystallographic study. The data collection within 6° ≤ 2θ ≤ 56° was carried out on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 20°C. An ω scan mode was used with a scan interval of 1.0° for -7 ≤ *h* ≤ 7, 0 ≤ *k* ≤ 14, 0 ≤ *l* ≤ 8. The different intensities were corrected for Lorentz and polarization effects. No decay was observed. An experimental absorption correction was applied, based on azimuthal scans of three reflections, with transmission factors from 0.428 to 0.998. The structure was solved by direct methods with SIR92 (6) and refined by full-matrix

TABLE 3
Interatomic Distances (Å) and Bond Angles (°)

Sn	Sn(OH) ₆ Octahedron							
	O(1)	O(1a)	O(2)	O(2a)	O(3)	O(3a)		
O(1)	2.069(2)							
O(1a) ^a	180.0	2.069(2)						
O(2)	94.09(10)	85.91(10)	2.051(3)					
O(2a) ^a	85.91(10)	94.09(10)	180.0	2.051(3)				
O(3)	87.76(11)	92.24(11)	88.22(11)	91.78(11)	2.056(3)			
O(3a) ^a	92.24(11)	87.76(11)	91.78(11)	88.22(11)	180.0	2.056(3)		
Sr	Sr(OH) ₈ Triangulated Dodecahedron							
	O(1)	O(1b)	O(2b)	O(2c)	O(3b)	O(3c)	O(4)	O(4a)
O(1)	2.741(3)							
O(1b) ^b	80.81(7)	2.693(3)						
O(2b) ^c	70.41(8)	90.44(8)	2.612(3)					
O(2c) ^d	128.51(8)	64.20(8)	73.24(9)	2.588(3)				
O(3b) ^c	99.03(8)	153.52(8)	65.11(8)	97.36(8)	2.699(3)			
O(3c) ^e	156.15(8)	119.79(8)	117.79(8)	74.45(8)	68.26(10)	2.699(3)		
O(4)	70.69(9)	124.10(8)	118.54(9)	160.78(9)	76.39(9)	86.39(9)	2.493(3)	
O(4a) ^b	100.84(8)	68.89(8)	158.88(8)	100.16(9)	136.01(8)	78.15(8)	73.88(6)	2.671(3)

O–H bond lengths are 0.82

Note. Atoms related by (a) -*x*, -*y*, -*z*; (b) *x*, 0.5 - *y*, 0.5 + *z*; (c) *x*, 0.5 - *y*, -0.5 + *z*; (d) -*x*, 0.5 + *y*, -0.5 - *z*; (e) 1.0 + *x*, 0.5 + *y*, 0.5 - *z*.

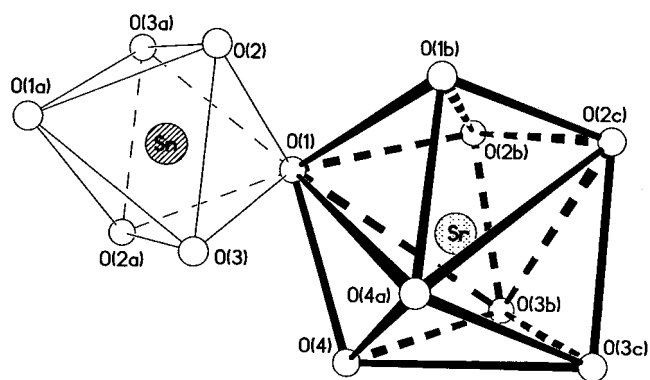


FIG. 1. Six- and eight-coordination of Sn and Sr atoms for $\text{Sr}_2\text{Sn}(\text{OH})_8$.

least-squares on F_0^2 using all the 897 independent reflections and 52 parameters (for 972 data collected). Final agreement factors are $R_1 = 0.0250$ and $wR_2 = 0.0541$ for all data. Anisotropic thermal displacement factors were assigned to all atoms. The hydrogen atoms were first located in the Fourier map, then fixed and refined as riding model on the oxygens. The final difference electron density map shows the highest peak and deepest hole as 1.056 and $-1.194 \text{ e } \text{\AA}^{-3}$, respectively. All calculations were performed using SHELX-97 (7). Crystallographic data and refinement parameters for $\text{Sr}_2\text{Sn}(\text{OH})_8$ are summarized in Table 1, atomic coordinates in Table 2.

RESULTS AND DISCUSSION

The known structures of hydroxo stannate all contain $\text{Sn}(\text{OH})_6$ octahedra and include $M\text{Sn}(\text{OH})_6$ with bivalent

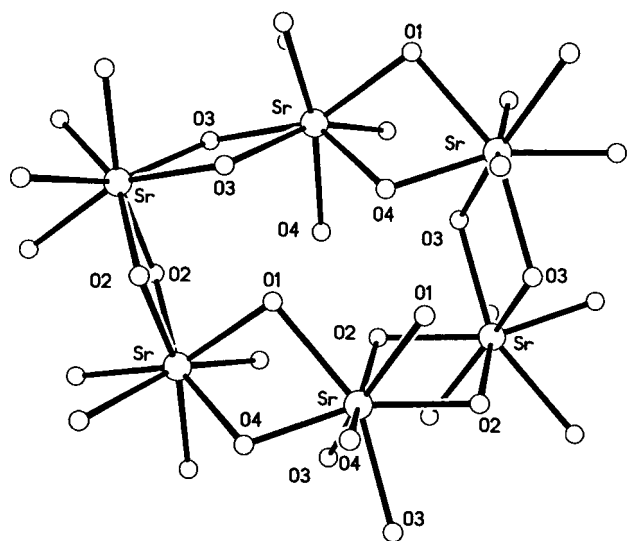


FIG. 2. View of the six-membered ring of $\text{Sr}(\text{OH})_8$ dodecahedra.

cations such as Mg (8), Ca (8, 9), Fe (8), Co (8), Mn (8, 10), Zn (9), and Cu (11); $M_2[\text{Sn}(\text{OH})_6] \cdot x\text{H}_2\text{O}$, with monovalent cations (for $x = 0$ Na, K (12) and for $x = 2$ Li (13)); and a two-dimensional layered compound, $\text{Ba}_2\text{SnO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ (14).

The structure of $\text{Sr}_2\text{Sn}(\text{OH})_8$ is a new three-dimensional framework of $\text{Sn}(\text{OH})_6$ octahedra and $\text{Sr}(\text{OH})_8$ dodecahedra. The tin atoms are six-coordinated with O(1), O(2), and O(3) (and their related atoms by symmetry) as illustrated in Fig. 1 (see Table 3 for the interatomic distances and bond angles). $\text{Sn}(\text{OH})_6$ forms an octahedron with an average Sn–O bond length of $2.059(8) \text{ \AA}$, within the values reported in the literature (8–14). Each $\text{Sn}(\text{OH})_6$ octahedron

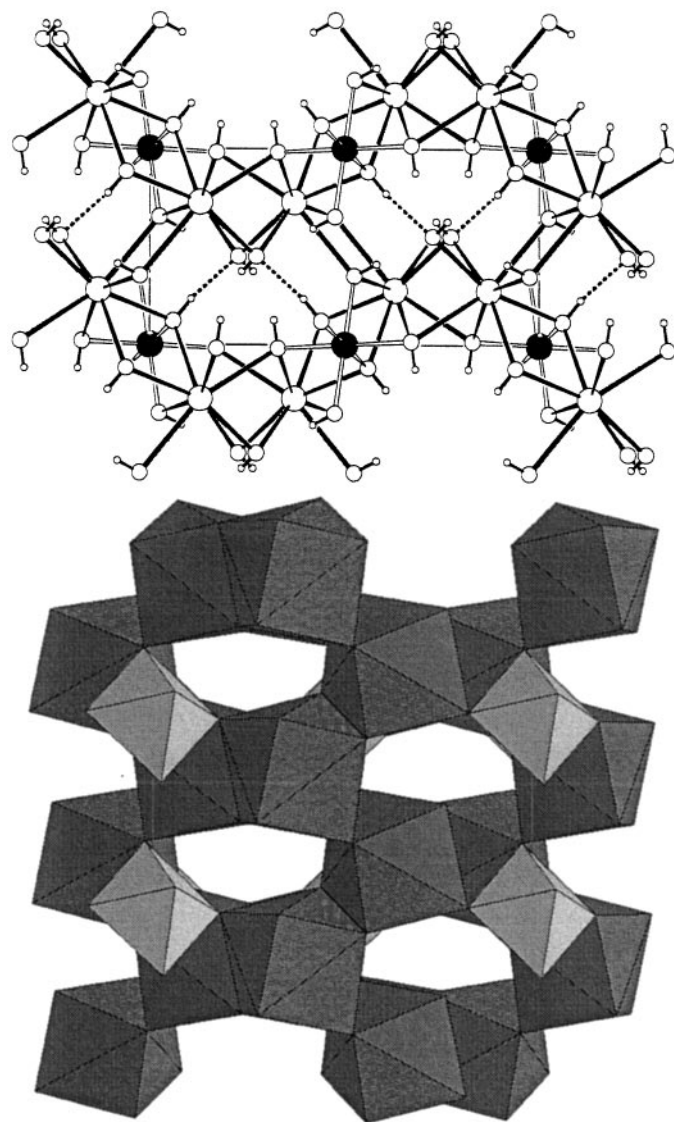


FIG. 3. Packing drawing for $[\text{Sr}(\text{OH})_{6/3}(\text{OH})_{2/2}]_2[\text{Sn}(\text{OH})_{6/3}]$ view down the c axis, showing (top) a molecular view with the hydrogen bonds dotted (Sr, large open circle; Sn, large filled circle) and (bottom) the filling of polyhedra (omitting the hydrogens) with the apparent channel along $[001]$.

is surrounded by eight Sr(OH)₈ polyhedra, four by corner sharing and four by edge sharing, related by the inversion center on the central Sn atom. The distances from the Sn atom to the surrounding eight Sr atoms range from 3.71(1) Å for the four edge-sharing Sr(OH)₈ polyhedra to 4.34(2) Å for the four corner-sharing ones. There are no OH bridges between two Sn(OH)₆ octahedra. The strontium atoms are coordinated by eight oxygens [two each of O(1), O(2), O(3), and O(4)] to an unusual triangulated dodecahedron (or bisdisphenoid) (shown in Fig. 1), a geometry rarely found in strontium and tin compounds. The Sr(OH)₈ dodecahedron shares edges with four other Sr(OH)₈ and two Sn(OH)₆ polyhedra, and shares corners with two other Sn(OH)₆ octahedra. The Sr–O distances range within the observed values for strontium hydroxides/hydrates (15), with Sr–O(4) in the lower limit. The shortest distances between the two Sr atoms are 4.057(3) and 4.174(3) Å. The O(4) is bridging and bonded only to Sr with distances of 2.493(3) and 2.671(3) Å. Analysis of the distances between the unique O(4) and the other oxygens shows only one hydrogen bond of 2.672(3) Å with O(2). All the other O···O contacts are above 2.85 Å, excluding any other strong hydrogen bonds. O(1), O(2), and O(3) are three-coordinated with two Sr atoms and one Sn atom, respectively. Valence sum calculation clearly indicated that O(1) and O(3) atoms

belong to OH groups (16). The valence sum analysis on O(2) atoms and O(4) atoms confirms the hydrogen bond link O(4)···H(2)O(2) as described above. Six Sr(OH)₈ dodecahedra form a six-membered ring connected by double oxygen bridges as shown in Fig. 2. These rings pack along the [001] direction, alternating with Sn(OH)₆ octahedra as illustrated in Fig. 3. The apparently empty channels are indeed filled with in-pointing hydrogens of the hydroxo groups, as shown in Fig. 3 (top), where the hydrogen bonds between O(4) and O(2) (dotted lines) are also evident. From the packing of the polyhedra and the oxygens' connectivity, the overall structure can be summarized as [Sr(OH)_{6/3}(OH)_{2/2}]₂[Sn(OH)_{6/3}] ([bisdisphenoid]₂[octahedra]). Compared with the known alkaline earth stannate materials, the title compound is the first compound built up by six-membered rings of Sr(OH)₈ dodecahedra.

The IR spectra of Sr₂Sn(OH)₈ show absorption bands typical for hydroxo groups [$\nu(\text{OH})$ (3385s, 3490vs, 3385s cm⁻¹), $\delta(\text{MOH})$ (1209m cm⁻¹), $\delta(\text{M}-(\text{OH})-\text{M})$ (954m cm⁻¹), and $\nu(\text{MO})$ (512vs, 858s cm⁻¹)] and the presence of water molecules could be ruled out due to the lack of the HOH bending mode near 1600 cm⁻¹ (17).

The experimental X-ray powder diffraction (XRPD) patterns of the elongated crystals and of the powder samples are all in agreement with the simulated XRPD pattern (see

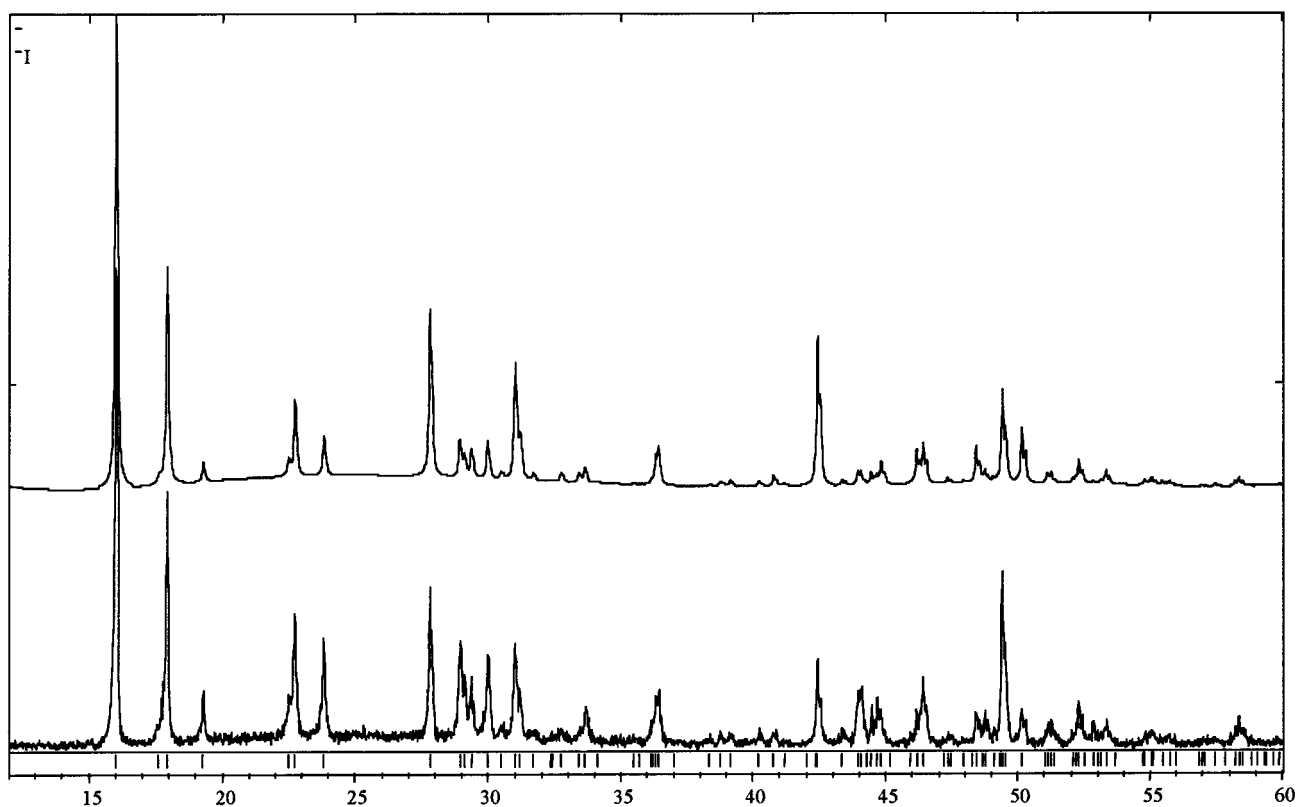
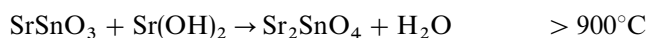
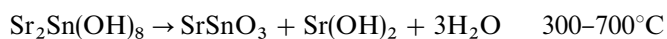


FIG. 4. Observed (bottom) and simulated (top) XRPD patterns for Sr₂Sn(OH)₈.

Fig. 4). Thermal analysis showed three steps corresponding to a weight loss of about 10% from 250 to 310°C, 4% from 310 to 500°C, and 2% from 500 to 700°C. These weight losses are attributable to the water molecules corresponding to about 2.5 H₂O, 1.0 H₂O, and 0.5 H₂O, respectively. We followed the temperature decomposition with XRPD and below 200°C we observed the original compound; from 300–700°C the crystalline phase was identified as cubic SrSnO₃ perovskite (18), while above 900°C it was identified as pure Sr₂SnO₄ oxide (19), in agreement with the total loss of four water molecules from Sr₂Sn(OH)₈. The TGA and XRPD analyses suggested the following decomposition processes in air:



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