

Synthesis and characteristics of a new three-dimensional molybdoantimonate $\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$

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Abstract

A novel three-dimensional compound of $\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$ has been synthesized by hydrothermal methods and structurally characterized by X-ray crystallography. It crystallizes in the triclinic system space group $P\bar{1}$ with $a = 11.574(2)$ Å, $b = 12.594(3)$ Å, $c = 13.277(3)$ Å, $\alpha = 94.59(3)^\circ$, $\beta = 112.68(3)^\circ$, $\gamma = 92.97(3)^\circ$, $V = 1772.7(6)$ Å³, $Z = 2$, $R_1 = 0.0275$, $wR_2 = 0.0984$ for 7364 unique reflections with $I > 2\sigma(I)$. The molecular structure is built up of Mo_6O_{21} , MoO_4 units, and cage-like units that contain 12 Sb atoms. IR, UV–Vis DRIS (Ultraviolet–Visible Diffuse Reflection Integral Spectrum), fluorescent spectra, and the thermogravimetric analysis of this compound were investigated.

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Keywords: Hydrothermal synthesis; Molybdoantimonate; Crystal structure; Photoluminescence

1. Introduction

Great efforts have been made for the discovery of microporous solids due to their rich structural chemistry and wide application in some commercial purposes as ion exchangers, absorbents, and catalysts [1]. Since many of the properties of porous materials depend on their composition and architecture, recent attention has focused on incorporating other main group and transition metals into open frameworks, and many materials have been reported to contain polyhedra such as $[\text{XO}_3]$, $[\text{XO}_4]$, $[\text{XO}_5]$, and $[\text{XO}_6]$ units [2–4]. Among these, a few open-framework antimony molybdates are reported.

Owing to the flexible interpolyhedral linkages and the variety of different coordination geometries about Sb^{III} , V and Mo^{VI} , molybdoantimonates such as $\text{K}_5\text{H}_2\text{SbMo}_6\text{O}_{24} \cdot (\text{H}_2\text{O})_7$ [5] and $M\text{SbMo}_2\text{O}_8$ ($M = \text{K}$, Li , Cu) [6–8] show good structural complexity and diversity. Since the lone pair of electrons of $\text{Sb}(\text{III})$ often lead to very distorted polyhedra, we undertook a synthetic and structural study on the antimony molybdates. To the best of our knowledge, most of them are synthesized either in solution with the temperature below 100°C or by solid-state reaction. Recently, we reported a molybdiantimonate NaSbMoO_5 which contains 5×6 Å channels along the c -axis by hydrothermal method [9]. In the present work, we introduce the synthesis and structure of a novel three-dimensional open-framework molybdiantimonate $\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$ (1). In addition, IR, UV–Vis DRIS (Ultraviolet–Visible Diffuse Reflection Integral Spectrum), fluorescent spectra, and the thermogravimetric analysis of the title compound were studied.

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2. Experimental section

2.1. Hydrothermal synthesis

A mixture of SbCl_3 (0.23 g, 1 M), tetrabutylammonium bromide (0.3 g, 1 mmol), Na_2MoO_4 (1 g, 4 mmol), and $\text{Ni}(\text{OAc})_2$ (0.3 g, 1 mmol) was dissolved in 8 ml distilled water. The pH value was adjusted to 8–9 by adding 1 M NaOH solution. This was sealed in a 15 ml Teflon-lined steel autoclave with 60% filling and heated at 180 °C for 48 h, and then cooled to room temperature. The resulting brown crystals accompanied with brown powder were filtered, the crystals were carefully selected, and washed with distilled water for single crystal X-ray diffraction.

2.2. X-ray crystallography

A single crystal with dimensions of $0.50 \times 0.20 \times 0.10$ mm was mounted on a glass fiber. The reflection intensities were collected on a Rigaku Weissenberg IP diffractometer. Lp corrections and an ψ empirical absorption correction were made for the intensity data. All molybdenum and antimony atoms were determined by direct method. The remaining atoms were located and refined by the usual procedure of a combination of the difference Fourier synthesis and the least-squares technique. The final $R = 0.0275$ and $wR = 0.0984$ ($w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$). All calculations were performed on a computer with the SHEXLT-PC program package [10,11].

A summary of crystal data and structure refinement for compound 1 is provided in Table 1. The atomic

coordinates and equivalent isotropic displacement parameters for 1 are given in Table 2. The selected bond lengths are listed in Table 3. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters were available in supplementary crystallographic data (CSD reference number: 414454).

2.3. Physical measurement

The IR spectra were recorded in the 4000–400 cm^{-1} region by using KBr pellet on a Nicolet Magna 750 FT-IR spectrophotometer. The UV-Vis DRIS spectrum was recorded on a Perkin-Elmer Lambda 900 UV-Vis spectrometer. The fluorescent spectra were recorded with an Edinburgh Instrument F920 fluorescent spectrometer using Xe lamp. The thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851e analyzer in air atmosphere with a heating rate of 15 °C/min from 40 to 1000 °C.

3. Results and discussion

3.1. Structure description

The asymmetric unit (Fig. 1) of $\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$ has 58 independent atoms. Sb(12) and Sb(13), Na(3) and Na(4) are statistically distributing. Only Sb(12) and Na(3) are considered in this paper for clarity. According to Adair et al. [12], Sb–O bond lengths are divided into three types: (1) the shortest one of 2.1 Å, (2) the intermediate of 2.6 Å, and (3) the longest up to 3.0 Å, which is a little shorter than the sum of van der Waals radii. In this paper, we use $L_{\text{max}}(2.65 \text{ Å})$ for $\text{Sb}^{\text{III}}\text{--O}$ by Donnay and Allmann to define the coordination environment of the 12 Sb^{III} atoms in the asymmetric unit. Thus, the structure is composed of four SbO_3 trigonal pyramids and eight SbO_4 distorted ψ trigonal bipyramids with the lone pair of electrons occupying equatorial positions. It was worth noting that the 12 independent Sb atoms constitute three edge-sharing hexahydric rings and take the shape of a cage (Fig. 2). Each ring comprises six Sb atoms. And at the center of each ring exists one Na^+ cation (Na1, Na2, and Na5), balancing the negative charge of the cage with the Na–O bond distance ranging from 2.167(3) to 2.756(4) Å.

Mo(1), Mo(2), and Mo(3) are six-fold coordinated by O atoms with the Mo–O bond distances in the range of 1.694–2.428 Å. Each MoO_6 octahedron contains one terminal vertex; the Mo–O_t (terminal atoms) distances are noticeably shorter than the Mo–O_b (bridging atoms) ones. Through central symmetrical operation (-1), the unit of $[\text{Mo}_6\text{O}_{21}]$ is formed by the edge-sharing

Table 1
Summary of crystal data and refinement results

Structural formula	$\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$
Formula weight	2592.66
Space group	$P\bar{1}$
Unit-cell dimension	$a = 11.574(2) \text{ Å}$, $b = 12.594(3) \text{ Å}$ $c = 13.277(3) \text{ Å}$, $\alpha = 94.59(3)^\circ$ $\beta = 112.68(3)^\circ$, $\gamma = 92.97(3)^\circ$
V (Å^3)	1772.7(6)
Z , ρ_{calc} (g cm^{-3})	2, 4.857
T (K)	293(2)
μ ($\text{MoK}\alpha$, mm^{-1})	1.0835
θ (deg)	$1.63 < \theta < 27.49$
Num. of collected data	8074
Num. of observed data ($I > 2\sigma(I)$)	7364
Num. of variables	524
Final R factors ($I > 2\sigma(I)$)	$R_1 = 0.0275$, $wR_2 = 0.0984$
Final R factors (all data)	$R_1 = 0.0329$, $wR_2 = 0.1095$
GOF	0.915
$(\Delta/\sigma)_{\text{max}}$	0.003
Largest diff. peak and hole	1.417, -1.272

Table 2
Atomic coordinates and anisotropic displacement parameters for compound 1

Atom	x	y	z	U (eq)	Atom	x	y	z	U (eq)
Sb(1)	5408(1)	4552(1)	3273(1)	12(1)	O(12)	7646(5)	5214(4)	3319(5)	35(1)
Sb(2)	2282(1)	7808(1)	-4666(1)	13(1)	O(13)	4191(4)	10772(3)	-5185(4)	14(1)
Sb(3)	4348(1)	8786(1)	581(1)	14(1)	O(14)	6033(5)	7911(4)	-6257(4)	19(1)
Sb(4)	785(1)	12370(1)	-5200(1)	14(1)	O(15)	1688(4)	10921(3)	-4765(4)	19(1)
Sb(5)	1129(1)	8668(1)	508(1)	13(1)	O(16)	2834(4)	8106(4)	727(4)	19(1)
Sb(6)	-1206(1)	8036(1)	-2282(1)	15(1)	O(17)	2197(5)	9516(4)	-7021(4)	25(1)
Sb(7)	6550(1)	6705(1)	2018(1)	14(1)	O(18)	281(4)	11779(4)	-6743(4)	19(1)
Sb(8)	-2297(1)	5319(1)	-3319(1)	15(1)	O(19)	-1135(5)	6482(4)	-2294(5)	26(1)
Sb(9)	4721(1)	8058(1)	-2014(1)	13(1)	O(20)	1041(5)	4211(4)	-1027(5)	33(1)
Sb(10)	-380(1)	3287(1)	-2090(1)	15(1)	O(21)	3987(5)	8043(3)	-866(4)	16(1)
Sb(11)	2655(1)	4102(1)	194(1)	14(1)	O(22)	7117(4)	7386(4)	-4141(4)	21(1)
Sb(12)	3565(2)	6684(1)	1782(1)	18(1)	O(23)	6341(5)	5735(3)	710(4)	18(1)
Sb(13)	3612(12)	6417(8)	1953(10)	16(2)	O(24)	5235(4)	5730(3)	2275(4)	13(1)
Mo(1)	3323(1)	10706(1)	-3934(1)	11(1)	O(25)	3086(4)	9260(3)	-4750(4)	16(1)
Mo(2)	3699(1)	9417(1)	-6125(1)	12(1)	O(26)	2796(4)	5678(3)	435(4)	17(1)
Mo(3)	5501(1)	7468(1)	-4904(1)	12(1)	O(27)	4891(4)	7327(3)	1236(4)	14(1)
Mo(4)	1178(1)	5537(1)	-3211(1)	14(1)	O(28)	2968(4)	8043(4)	-3065(4)	19(1)
Mo(5)	7979(1)	8990(1)	821(1)	15(1)	O(29)	9106(7)	9194(6)	2115(5)	56(2)
O(1)	513(4)	8154(4)	-1040(4)	18(1)	O(30)	3808(4)	7998(3)	-6035(4)	18(1)
O(2)	-724(6)	13550(4)	-5755(4)	30(1)	O(32)	681(4)	8467(3)	-4883(4)	16(1)
O(3)	807(5)	7245(4)	901(4)	23(1)	O(31)	3249(5)	10501(4)	-2714(4)	24(1)
O(4)	5278(4)	3490(3)	2013(4)	17(1)	O(33)	-1604(5)	4328(4)	-2195(4)	22(1)
O(5)	2809(6)	9837(4)	-429(5)	36(1)	O(34)	3555(5)	4489(4)	2689(4)	26(1)
O(6)	1763(5)	6284(4)	-1930(4)	22(1)	O(35)	4898(5)	7551(4)	-3856(4)	22(1)
O(7)	4662(5)	9670(4)	-6870(4)	19(1)	Na(1)	6040(3)	3864(2)	668(2)	20(1)
O(8)	6908(6)	7907(4)	713(5)	37(1)	Na(2)	1840(3)	8245(2)	-1966(2)	20(1)
O(9)	-114(6)	4658(4)	-3361(5)	31(1)	Na(3)	9966(10)	9834(8)	3907(8)	36(2)
O(10)	8716(6)	8636(5)	-59(5)	40(1)	Na(4)	10461(9)	9732(8)	3759(8)	30(2)
O(11)	4987(5)	6175(4)	-5516(4)	24(1)	Na(5)	684(3)	6133(2)	-761(2)	24(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The occupancy of Sb12, Sb13, Na3, and Na4 is 50%.

MoO₆ octahedral. And it can be derived from the β -[Mo₈O₂₆]⁴⁻ anion by removing two symmetrical MoO₆ octahedra (Fig. 3). Mo(4) and Mo(5) are tetrahedral, coordinated with the Mo–O bond lengths average 1.749 Å. The O–Mo–O bond angles are close to 109°, showing that the MoO₄ tetrahedron is relatively regular.

The cage-like units are connected into chains extending along the *a*-axis (Fig. 4) through μ_2 -O(24) and μ_3 -O(27) atoms, which combine with Sb(1), Sb(7), and Sb(12)' atoms and Sb(3), Sb(12), and Sb(7)' atoms, respectively. The Mo(4)O₄ tetrahedron is fixed in the center of the cage by Mo–O–Sb bonds. The three μ_2 -O atoms (O(10), O(8), and O(5)) combine with the Mo(5)O₄ tetrahedra and the cages along *a*- and *b*-axis, forming a layer along [001] (Figs. 4 and 5). And these layers are linked into a three-dimensional framework through [Mo₆O₂₁] units. From the projected view of [100], holes (4.8 × 5.0 Å) can be seen in the cage units. And the Na⁺ cations (Na(1) and Na(5)) reside in these holes, indicating that the compound may be used as ion-exchange materials. But the lone pair of Sb(11) atom lies in the middle of these holes. This may affect the porosity of the compound.

3.2. Bond valence analysis

The bond valence sums (BVS) for the molybdenum and antimony atoms were calculated using parameters given by Brown and Wu [13]. The results are summarized in Table 4. The BVS for all molybdenum and antimony atoms are in agreement with their expected values.

3.3. Spectroscopy and thermal analysis

Similar to NaSbMo₅ [9], the IR spectra of the title compound exhibit the characteristic band of molybdoantimonates. But it is more intricate due to the complicated structure of the title compound. We present the assignments of the two compounds in Table 5. A strong band at 926–981 cm⁻¹ shows characteristics of ν as Mo–Ot (Ot, terminal O atoms), while features at 753–712 cm⁻¹ show characteristics of ν as Mo–O–Mo. The absorption band in the region of 630–530 cm⁻¹ shows the characteristic band of antimony oxides which result from stretching and bending vibrations [14,15]. The Sb–O stretching vibrations are enhanced as the ratio of the Sb:Mo in the title compound is larger.

Table 3
Selected bond distances (Å) for compound 1

Bond	Dist.	Bond	Dist.
Sb(1)–O(34)	1.975(5)	Sb(11)–O(20)	1.966(5)
Sb(1)–O(24)	2.033(4)	Sb(11)–O(23)#2	1.980(5)
Sb(1)–O(4)	2.009(5)	Sb(12)–O(27)	2.088(5)
Sb(2)–O(28)	1.951(5)	Sb(12)–O(16)	2.350(4)
Sb(2)–O(25)	2.039(4)	Sb(12)–O(26)	1.972(5)
Sb(2)–O(32)	1.998(4)	Sb(12)–O(24)	2.237(4)
Sb(3)–O(16)	1.994(5)	Sb(13)–O(26)	1.990(14)
Sb(3)–O(5)	2.326(5)	Sb(13)–O(24)	2.018(12)
Sb(3)–O(21)	1.948(4)	Sb(13)–O(27)	2.345(12)
Sb(3)–O(27)	2.117(4)	Mo(1)–O(31)	1.694(5)
Sb(4)–O(18)	1.969(5)	Mo(1)–O(14)#1	1.818(5)
Sb(4)–O(15)	2.158(4)	Mo(1)–O(15)	1.834(5)
Sb(4)–O(32)#3	1.995(4)	Mo(1)–O(25)	1.992(4)
Sb(4)–O(2)	2.292(5)	Mo(1)–O(13)	2.252(5)
Sb(5)–O(1)	1.939(5)	Mo(1)–O(7)#1	2.253(5)
Sb(5)–O(16)	2.053(5)	Mo(2)–O(17)	1.704(5)
Sb(5)–O(3)	1.963(4)	Mo(2)–O(7)	1.784(5)
Sb(6)–O(18)#3	1.992(5)	Mo(2)–O(30)	1.808(4)
Sb(6)–O(22)#5	2.519(5)	Mo(2)–O(13)	1.951(4)
Sb(6)–O(19)	1.962(5)	Mo(2)–O(25)	2.217(4)
Sb(6)–O(1)	2.025(4)	Mo(2)–O(13)#1	2.429(4)
Sb(7)–O(23)	1.968(5)	Mo(3)–O(11)	1.727(5)
Sb(7)–O(24)	2.052(4)	Mo(3)–O(22)	1.764(5)
Sb(7)–O(27)	2.032(4)	Mo(3)–O(35)	1.779(5)
Sb(7)–O(8)	2.525(6)	Mo(3)–O(30)	2.137(5)
Sb(8)–O(34)#6	1.955(5)	Mo(3)–O(13)#1	2.212(4)
Sb(8)–O(33)	1.976(4)	Mo(3)–O(14)	2.213(5)
Sb(8)–O(19)	1.968(5)	Mo(4)–O(6)	1.740(5)
Sb(9)–O(4)#2	1.949(4)	Mo(4)–O(12)#2	1.741(5)
Sb(9)–O(21)	2.012(5)	Mo(4)–O(9)	1.751(5)
Sb(9)–O(28)	1.968(5)	Mo(4)–O(2)#3	1.800(5)
Sb(9)–O(35)	2.566(5)	Mo(5)–O(29)	1.698(6)
Sb(10)–O(33)	1.953(5)	Mo(5)–O(10)	1.736(6)
Sb(10)–O(20)	1.950(5)	Mo(5)–O(8)	1.753(5)
Sb(10)–O(3)#6	1.980(5)	Mo(5)–O(5)#4	1.784(5)
Sb(11)–O(26)	1.973(4)		

Symmetry code: #1 $-x+1, -y+2, -z$; #2 $-x+1, -y+1, -z$; #3 $-x, -y+2, -z-1$; #4 $-x+1, -y+2, -z$; #5 $x-1, y, z$; #6 $-x, -y+1, -z$.

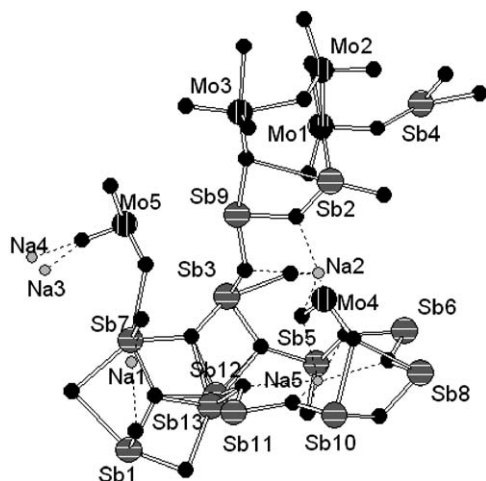


Fig. 1. The asymmetric unit of $\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$.

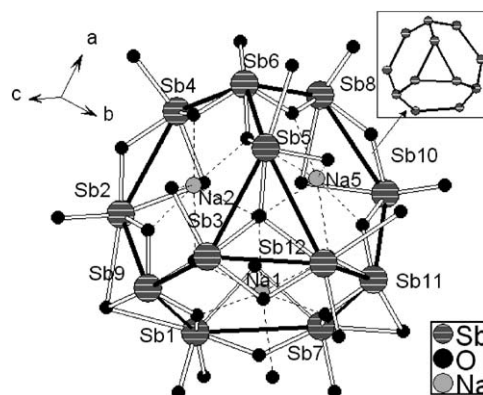


Fig. 2. Twelve independent Sb atoms that constitute three edge-sharing hexahydric rings.

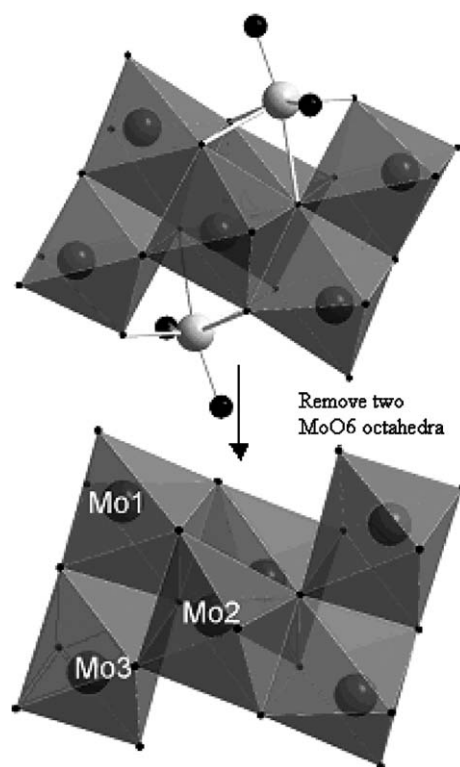


Fig. 3. $[\text{Mo}_6\text{O}_{21}]$ unit of the title compound derived from the β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion.

The absorption band from 350 to 800 nm in the UV–Vis DRIS spectrum is consistent with the color of the compound. The λ_{max} at 380 nm can be assigned to the $\text{O} \rightarrow \text{M}$ LMCT transfer transition. The fluorescent emission spectrum of the title compound (Fig. 6) in the solid state at room temperature shows that the range of the emission band is from 300 to 500 nm with the peak at 390 nm. The full-width at half-maximum of the emission peak is about 65 nm. The peak of the excitation band is at 250 nm. The result is similar to the

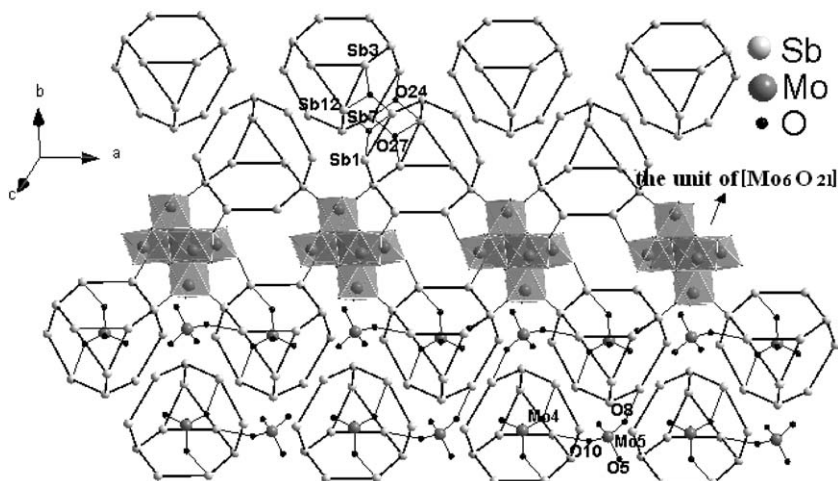
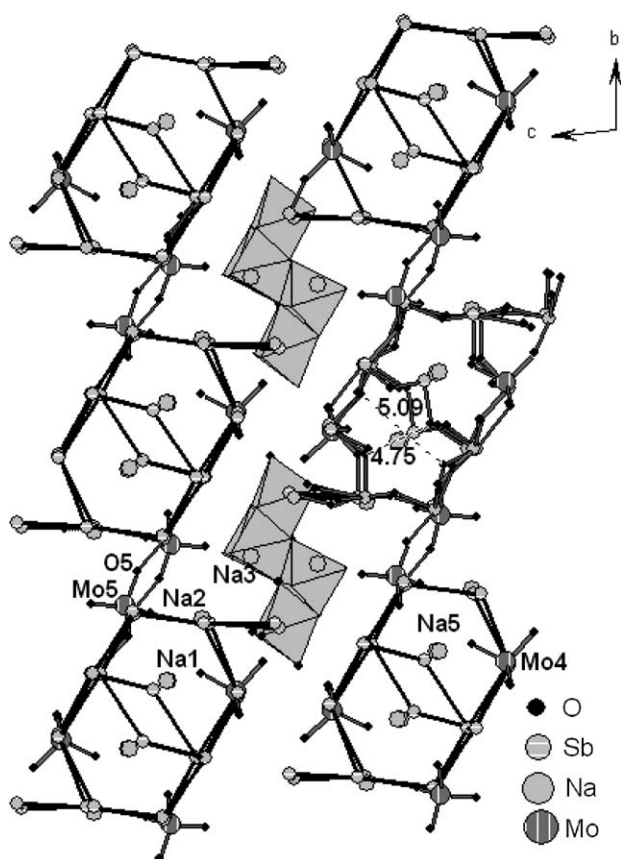


Fig. 4. Packing of the chains built up of cage-like units of 12 Sb atoms.

Fig. 5. Layers that are linked into three-dimensional framework through $[\text{Mo}_6\text{O}_{21}]$ units.

photoluminescence characteristics of the Sb^{3+} -doped SrPO_4 [16], of which the emission peak is at 396 nm. According to it, the ground state of Sb^{3+} ($5s^2$) is $^1\text{S}_0$. The excited states configuration ($5s5p$) results in the triplet level $^3\text{P}_0$, $^3\text{P}_1$, $^3\text{P}_2$, and a singlet level $^1\text{P}_1$. The excitation band at 250 nm should be attributed to the

Table 4
The BVS for compound 1

Atom	Valence	Atom	Valence
Sb1	2.90 +	Sb10	2.90 +
Sb2	2.94 +	Sb11	2.69 +
Sb3	2.78 +	Sb12	2.62 +
Sb4	3.02 +	Mo1	5.73 +
Sb5	2.54 +	Mo2	5.88 +
Sb6	2.80 +	Mo3	5.78 +
Sb7	2.86 +	Mo4	5.75 +
Sb8	2.84 +	Mo5	6.39 +
Sb9	2.46 +		

Table 5
Assignments (cm^{-1}) of NaMoSbO_5 and compound 1

Assignments	NaMoSbO_5	Compound 1
$\nu_{\text{as}}(\text{Mo}=\text{O}_t)$	926 (s)	926 (m)
	902 (s)	902 (m)
	890 (s)	861 (m)
	819 (s)	830 (sh, s)
		806 (br, s)
$\nu_{\text{as}}(\text{Mo}-\text{O}_b)$	753 (s)	779 (m)
		753 (s)
$\nu_{\text{as}}(\text{Sb}-\text{O}_b)$	712 (s)	711 (s)
	629 (s)	666 (sh, s)
		637 (sh, s)
		610 (br, vs)
$\nu(\text{Sb}-\text{O}_b)$	535 (s)	462 (s)

Vs = very strong; s = strong; m = middle; sh = shoulder; br = broad.

$^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition. And the emission band around 390 nm should be assigned to the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition of the Sb^{3+} . The thermogravimetric analysis showed that the structure remains stable up to 600 °C. The weight

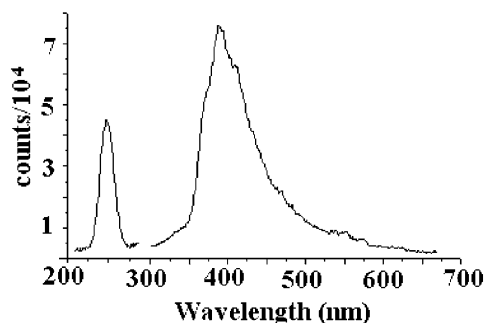


Fig. 6. Photoluminescent spectra of compound 1 measured at room temperature. For emission measurement, the excitation wavelength was 250 nm, while for excitation measurement, the emission wavelength was 390 nm.

loss in the temperature range from 600 to 1000 °C can be ascribed to the decomposition of the starting oxide and the evolution of Na and/or Sb single oxides. (The decomposition temperature of Sb_2O_3 is 635 °C according to the phase diagram [17].) This compound may find widespread application in blue-light-emitting devices because of its thermal stability and insolubility.

4. Conclusions

In summary, a novel compound, $\text{Na}_4\text{Sb}_{12}\text{Mo}_5\text{O}_{35}$, crystallizes in a new type of structure not previously encountered. To our knowledge, open-framework molybdoantimonates usually take a layered structure such as $M\text{Sb}^{\text{III}}\text{Mo}_2\text{O}_8$ ($M = \text{Cu}, \text{K}, \text{Li}$) and NaSbMoO_5 . It takes a three-dimensional structure composed of Mo_6O_{21} , MoO_4 units and cage-like units that contain 12 Sb atoms. The holes ($4.8 \times 5.0 \text{ \AA}$) along [100] in the structure indicate that the compound may be used as ion-exchange material. The fluorescent spectrum of the compound was measured in solid state at room temperature. On excitation at 340 nm, this molybdoantimonate showed an emission band with $\lambda_{\text{max}} = 390 \text{ nm}$.

Acknowledgments

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