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Reexamination of the Crystal Structure of $Na_3Sb_7O_9Se_3 \cdot Sb_{0.319}(H_2O,OH)_3$

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The crystal structure of $Na_3Sb_7O_9Se_3 \cdot Sb_{0.319}(H_2O,OH)_3$ has been determined using a single crystal prepared by hydrothermal synthesis to a conventional $R=0.043$, $R_w=0.039$ for 1556 reflections. It is hexagonal with a space group of $P6_3$; $a=14.422(4)$, $c=5.5448(8)$ Å, $Z=2$. The structure consists of infinite tunnels formed by the linkages of SbO_3 pyramids. $SbSe_3$ pyramids among the tunnels connect the tunnels to form a three-dimensional structure. Na atoms were on the inside wall of the tunnel. It was revealed that statistically occupied $Sb(H_2O,OH)_6$-octahedra are located at the center of the tunnel. Two statistical sites for the Sb atom of the $SbSe_3$ pyramids are pointed out.

Oxide sulfides exhibit unique structures, in which oxygen and sulfur atoms have direct bondings to cations individually without forming molecular ions, such as SO_4^{2-}. Since the chemical behaviors of oxygen and those of sulfur are significantly different from each other, it is interesting to clarify the difference in the characters of these atoms in a crystal structure of oxide sulfide.

So far the crystal structures of two synthetic compounds and a natural mineral have been reported for oxide sulfides of alkaline metals and antimony with a general formula, $A_3Sb_7O_9S_3 \cdot X$, where A = alkaline metal, e.g. $K_3Sb_7O_9S_3$,[1)] $Na_3Sb_7O_9S_3 \cdot Na_{0.5}(H_2O,OH)_3$,[2)] and cetineite: $K_3Sb_7O_9S_3 \cdot Na_{0.5}(H_2O,OH)_3$.[2)] Moreover, two reports on the crystal structure of the Se-analogue have appeared.[3,4)] All of the materials are hexagonal with the space group $P6_3$, $a \approx 14.5$, $c \approx 5.5$ Å. The common features of the structures are an infinite tunnel structure comprising corner-sharing Sb–O pyramids and Sb–S(Se) pyramids connecting the tunnels.

The first analysis of the crystal structure of the $A_3Sb_7O_9S_3 \cdot X$-type oxide sulfides was reported by Graf and Schäfer[1)] for $K_3Sb_7O_9S_3$. However, their X-ray analysis showed that the only atom existing inside of the Sb–O tunnel was the K atom. They assumed that the 2*a* site (Wyckoff notation), hereafter designated as the X site, which is located at the center of the tunnel structure, was vacant. Since bonding between the K ion and oxygen is largely ionic, it is unreasonable that the K cation has such an one-sided oxygen coordination as reported by Graf and Schäfer.[1)] Nakai and Katsura found that a difference Fourier synthesis in the structural analysis of $Na_3Sb_7O_9S_3$ gave a residual electron density at the X site.[2)] They assumed the presence of some atoms at the X site which may stabilize the alkaline ion. Furthermore, additional atoms were found at the center of the tunnel for the Se-analogue, $Na_3Sb_7O_9Se_3$.[3)] On the other hand, Kluger and Pertlik[4)] independently analyzed the crystal structure of $Na_3Sb_7O_9Se_3 \cdot [0.5Sb(OH)_3]$, and found the tunnel to be occupied by $Sb(OH)_3$ pyramids at the center with a half occupancy. Recently, Sabelli et al.[2)] reported the crystal structures of cetineite, $K_3Sb_7O_9S_3 \cdot Na_{0.5}(O,OH)_3$ and the synthetic Na-analogue, $Na_3Sb_7O_9S_3 \cdot Na_{0.5}(O,OH)_3$. They attributed this to the idea that the X site is occupied by an Na atom with a half occupancy, which is octahedrally surrounded by six O atoms of water molecules or hydroxyl groups. In addition, they found two statistical sites for the Sb site of the SbS_3 pyramid related by the pseudo-mirror plane perpendicular to the *c*-axis.

In the present study, the crystal structure of $Na_3Sb_7O_9Se_3 \cdot X$ was reinvestigated in order to examine these unusual structure features; i. e., the existence of certain atoms at the center of the tunnel structure, an $Sb(OH)_3$ pyramid, an $(Na, \square)(H_2O, OH)_6$ octahedron or the other, and the splitting of the Sb site of the $SbSe_3$ pyramid.

Experimental

The starting material for the preparation of single crystals was synthesized by a solid-state reaction in a silica-tube. A mixture of Na_2Se, Sb_2O_3, and Sb_2Se_3 in a molar ratio of 3 : 6 : 1 was sealed in a silica-tube, and was kept at 220 °C for 2 d. The single crystals were grown from the fine powder of the starting material with a 1%-NaOH aqueous-solution as the solvent in an Au capsule under the hydrothermal condition of 300 °C and 1000 atm. The crystals were identified by X-ray powder diffraction. A quantitative electron microprobe analysis of the crystal gave the following chemical composition: Na, 5.1; Sb, 63.1; Se, 17.1; O, 14.2 wt%.

A preliminary X-ray diffraction investigation of the crystals was carried out by using Weissenberg and precession cameras. A red single crystal with a prismatic hexagonal shape ($0.075 \times 0.070 \times 0.100$ mm^3) was mounted on a RIGAKU AFC-5 four-circle automated diffractometer. The lattice parameters, determined by a least-squares refinement of the 2θ values of 25 strong reflections, are $a=14.422(4)$, $c=5.5448(8)$ Å, and $Z=2$. The intensity data were collected with graphite-monochromatized Mo $K\alpha$ radiation generated by a Rotaflex RU-200 under the operating condition of 50 kV and 150 mA. A total of 2597 independent reflections were obtained using the 2θ–ω scanning mode at a scanning rate of 2° min^{-1} up to $2\theta=85°$. The intensity measurement was repeated for a reflection with $\sigma(|F_o|)/|F_o|$ larger than

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#Deceased on January 6, 1985.

0.05. The intensities of three standard reflections measured every 50 observations did not show any fluctuation larger than 2%. The data were corrected for Lorentz and polarization factors. An absorption correction was made with a computer program, ACACA[5] ($\mu=154.0$). The subsequent crystal structure analysis was carried out using 1556 reflections with the criteria that $|F_o|\geq 3\sigma(|F_o|)$.

Structure Analysis

The positions of the Sb1, Sb2, Sb3, Na, Se, O1, O2, and O3 sites in an initial model were determined using Patterson and Fourier syntheses referring to the crystal structure of $Na_3Sb_7O_9S_3 \cdot Na_{0.5}(H_2O,OH)_3$.[2] The structure was refined by a full-matrix least-squares program, RFINE2.[6] All of the scattering factors were taken from Cromer and Mann,[7] and anomalous dispersion factors from the International Tables for X-ray Crystallography, Vol. IV.[8] The observed structure factors, $|F_o|$, were weighted by the formula $1/\sigma^2(|F_o|)$. The statistical two site for the Sb1 site, which was found in the crystal structure of $Na_3Sb_7O_9S_3 \cdot Na_{0.5}(H_2O,OH)_3$,[2] was also observed in the Patterson and Fourier maps of the present Se-analogue compound. A difference Fourier synthesis after the isotropic refinement of all the sites mentioned above showed a relatively strong residual electron density peak at the X site, and twelve weak peaks at two independent sites, hereafter expressed as Ow sites (Owa and Owb), around the X site inside the tunnel-structure of Sb and O. However, a refinement with the scattering factor of the Na atom for the X site was unsuccessful. Then, anisotropic least-squares refinements using scattering factor of Sb(Model I) or Se(Model II) for the X site were carried out. The least-squares refinements for the two models were repeated until the shift/error of each parameter became less than 0.01 and 0.02, respectively. Both refinements converged at $R=0.043$ and $R_w=0.039$ for 1556 reflections. The final difference Fourier maps of the both models showed no peaks without a range of -2 to 4 e Å^{-3}. No significant difference was found between the two models in the final positional parameters larger than the estimated standard deviations, except for the z coordinates of the Owa sites. The z coordinate obtained by the refinement was 0.4769(26) for Model I and 0.2529(47) for Model II. The refined occupancy factors of the X site were 0.3194(4) and 0.470(5), respectively. The corresponding temperature factors of the two models did not show any significant differences. However, we have adopted Model I (X=Sb) as the final model for the following reasons. The interatomic distances between the X and Ow sites are within the range of 2.01 to 2.41 Å with an average of 2.20 Å for both models. These X–Ow distances are too long to be adopted as the Se–O distances. Furthermore, the atomic ratio derived from the electron microprobe analysis, Na : Sb : O : Se=3.00 : 7 : 12.0 : 2.91, indicated that Se was rather poor compared with the ideal ratio, 3 : 7 : 9 : 3 of the framework part, $Na_3Sb_7O_9Se_3$ which consists of the Sb–O tunnel, Sb–Se pyramid, and Na on the inside wall of the tunnel. This analytical result does not support the existence of excess Se at the X site. Since the refinement with a scattering factor of oxygen for the Ow sites with half occupancies converged with a reasonable temperature factor, the Ow sites were considered to be occupied by the oxygen atoms. The IR spectrum of the present sample showed absorption peaks of the O–H vibration bands at around 3300 cm^{-1}. Therefore, the O atoms in the Ow sites can be attriubuted to water molecules or hydroxyl groups, H_2O or OH^-. The interatomic distances between Owa and Owb, 1.62 and 1.77 Å, are too short for an O–O distance. Thus, these two sites can not be occupied simulataneously, and should be occupied statistically.

The final atomic positional parameters and equivalent isotropic temperature factor for Model I are given in Table 1. The anisotropic temperatue factors and the complete observed and calculated structure factors are deposited as Document No. 66055 at the Office of the Editor of Bull. Chem. Soc. Jpn. The interatomic distances and bond angles were calculated using a computer program, UMBADTEA.[9] The interatomic distances and selected bond angles are listed in Table 2.

Description and Discussion of the Structure

The present crystal structure analysis gave a structural formula of this compound to be $Na_3Sb_7O_9Se_3 \cdot Sb_x(H_2O,OH)_3$ with $x=0.319$ determined by occupancy refinement. The structure is illustrated in Fig. 1. It is found that the structure is basically isostructural with those of the other members of the $A_3Sb_7O_9S_3 \cdot X$ type compounds. Two SbO_3 pyramids of Sb2 and Sb3 share a corner at the O1 site to form a pair of pyramids. These pairs also share the O2 and O3 atoms with the neighboring pairs standing on the different z levels to make up an infinite tunnel structure around the 6_3-axis. The $SbSe_3$ pyramid is located among the three tunnel structures, which are connected by the Se–Na bondings to form a three dimensional framework. The Sb1 atom is statistically distributed between two sites, Sb1a and Sb1b, with an occupancy ratio of 57 : 43. Thus, two kinds of $SbSe_3$ pyramids in the opposite directions are statistically located in the structure (Fig. 1b). Similar arrangements of the SbS_3 pyramids are found in the crystal structures of cetineite and its synthetic Na-analogue.[2] The apparent separation distance of the two Sb1 sites is 1.794(3) Å in the present structure. This distance is too short for the Sb–Sb interatomic distance, and contradict the simulataneous occupation of Sb atoms at both the Sb1a and Sb1b sites, to support the statistical distribution of Sb atoms. This Sb1a–Sb1b distance is much longer than those observed in the crystal structures of cetineite and the synthetic Na-analogue.[2] This elongation can be attributed to a difference in the interatomic distance between Sb–Se and Sb–S in the $SbSe_3$ and SbS_3 pyramids, respectively.

Table 1. Positional Parameters and Equivalent Isotropic Temperature Factors, with Estimated Standard Deviations in Parentheses

	K[a)]	x	y	z	B_{eq}
Sb1a	0.57(2)	0.6667	0.3333	0.8376	1.65
Sb1b	0.43(2)	0.6667	0.3333	0.5506(5)	1.14
Sb2	1.0	0.43532(4)	0.15451(4)	0.2167(11)	1.55
Sb3	1.0	0.39612(4)	0.37393(4)	0.2127(11)	1.38
Sb$_X$	0.319(4)	0.0	0.0	0.4769(26)	1.25
Na	1.0	0.2926(3)	0.1832(3)	0.7117(53)	3.29
Se	1.0	0.52354(8)	0.36081(9)	0.6948(16)	3.17
O1	1.0	0.3429(5)	0.2181(5)	0.2215(43)	2.12
O2	1.0	0.3458(15)	0.0580(17)	0.4620(41)	2.68
O3	1.0	0.3406(17)	0.0552(16)	0.9554(34)	2.25
Owa	0.5	0.1078(14)	0.1244(13)	0.1804(53)	3.1(4)[b)]
Owb	0.5	0.1279(13)	0.0235(13)	0.1684(40)	2.8(4)[b)]

a) Occupancy. b) Isotropic temperature factors.

Table 2. Interatomic Distances (Å) and Bond Angles (°) with Estimated Standard Deviations in Parentheses

Sb1a–Se	2.494(3)×3	Sb1b–Se	2.424(2)×3	Se–Se	3.963(2)		
Sb2–O2	1.91(2)	Sb3–O3′	1.96(1)	O1–O2	2.69(1)	O1–O2′	2.75(1)
–O1	1.959(2)	–O2′	1.98(2)	O1–O3	2.76(1)	O1–O3′	2.64(1)
–O3	2.02(1)	–O1	1.980(1)	O2–O3	2.82(3)	O2′–O3′	2.74(3)
mean	1.96	mean	1.97				
Sb$_X$–Owb	2.01(3)×3	Owa–Owa	2.92(3)	Owa–Owb′	2.71(3)		
–Owa	2.03(2)×3	Owa–Owa′	3.25(1)	Owa–Owb′	2.85(3)		
–Owa′	2.36(3)×3	Owa–Owb	1.62(4)	Owb–Owb	2.95(4)		
–Owb′	2.41(3)×3	Owa–Owb	1.77(3)	Owb–Owb′	3.26(1)		
mean	2.20						
Na–Owa	2.42(3)						
–Owb	2.43(3)						
–O3	2.65(1)						
–O2	2.68(1)						
–O3′	2.72(1)						
–O2″	2.76(1)						
–O1	2.80(1)						
–O1′	2.90(1)						
–Se	3.022(1)						
Se–Sb1a–Se	105.2(2)×3	Se–Sb1b–Se	109.6(1)×3				
O1–Sb2–O2	87.8(3)	O1–Sb3–O2′	88.1(2)				
O1–Sb2–O3	88.0(2)	O1–Sb3–O3′	84.2(2)				
O2–Sb2–O3	91.4(6)	O2′–Sb3–O3′	88.3(6)				
Owa–Sb$_X$–Owa	76.6(10)×3	Owb–Sb$_X$Owb	75.2(11)×3				
Owa–Sb$_X$–Owa′	92.0(12)×3	Owb–Sb$_X$–Owb′	94.5(6)×6				
Owa–Sb$_X$–Owa″	95.3(5) ×6	Owb–Sb$_X$–Owb″	94.5(13)×3				

The sodium atoms are attached to the inside wall of the SbO_3 tunnel. The outside wall of the tunnel consists of Sb atoms, and the inside consists of the O atoms (Fig. 1a). Graf and Schäfer[1)] pointed out that such a biased configuration of cations and anions is stabilized by the alkaline ions. They also reported the possibility that zeolitic water may be located at the center of the tunnel after their measurements of the IR spectrum and weight loss under the condition of 130 °C and 10 Torr (1 Torr=133.322 Pa), although their structure analysis of $K_3Sb_7O_9S_3$ did not indicate any additional atoms inside the tunnel. Until now, two models have been proposed for the atomic group occupying the center of the tunnel, the X site: $Sb(OH)_3$ pyramid for $Na_3Sb_7O_9Se_3 \cdot X$[4)] and $(Na,\square)(H_2O, OH)_6$ octahedron for $K_3Sb_7O_9S_3 \cdot X$ (cetineite) and $Na_3Sb_7O_9S_3 \cdot X$.[2)] The Sb$_X$ site is surrounded by the three Ow atoms at a distance of 2.0 Å and three further Ow atoms at around 2.4 Å to form an $SbOw_6$ octahedron. Therefore, the atomic group in the tunnel structure can be attributed to $(\square, Sb)(H_2O,OH)_6$ octahedra, which are disordered in the two configurations, $Sb_X(Owa)_6$ and $Sb_X(Owb)_6$. The octahedra share the top and bottom triangular faces to form an infinite column along the 6_3-axis (Fig. 1b).

The octahedron at the center of the tunnel structure is quite distoreted with shorter and longer Sb$_X$–Ow distances (Table 2). Kluger and Pertlik[4)] described the coordination of Sb$_X$ (Sb4 in their literature) to be an

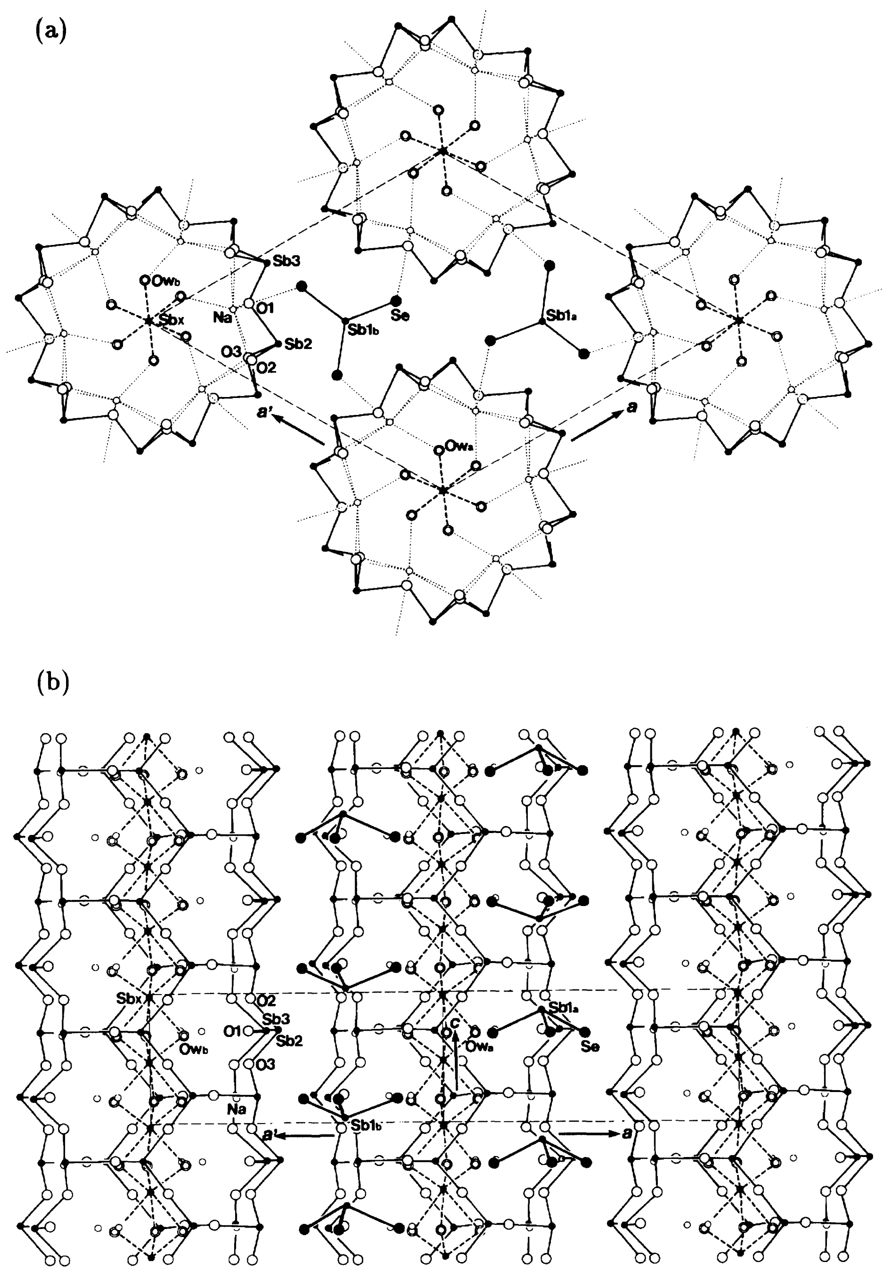

Fig. 1. Crystal structure of $Na_3Sb_7O_9Se_3{\cdot}Sb_{0.319}(H_2O, OH)_3$. (a) A (001) projection showing the connection of the tunnel structures by $SbSe_3$ pyramids and $(\square, Sb)(H_2O, OH)_6$ octahedra in the tunnels. (b) A (110) projection showing the infinite Sb_2O_3 tunnel frameworks and columns of $(\square, Sb)(H_2O, OH)_6$ octahedra inside them. The framework at (00*z*) is eliminated for the prominence for the statistically distributed Sb1–Se_3 pyramids. All of the cations are indicated by larger circles and anions by smaller ones. The solid lines indicate the Sb–Se and Sb–O bondings and the broken lines those of Sb–Ow; the fine broken lines show the edges of the unit cell. The bondings drawn by fine dot lines are omitted in (b) to avoid complexity.

$Sb(OH)_3$ pyramid with a shorter Sb_X–(OH) distance of 2.05 Å. The coordination polyhedra of the Sb_X sites in both models of Kluger and Pertlik[4] and of the present study are identical with each other. The introduction of the next neighboring three (OH) groups into the bondings to the Sb4 atom in the model by Kluger and Pertlik,[4] makes the coordination polyhedron to be an octahedron. However, the Sb_XOw_6 octahedron found in the present study is disordered. This is a marked difference between the two structures.

The crystallographic data, mean interatomic distances and bond angles for these $A_3Sb_7O_9(S, Se)_3{\cdot}X$ type compounds are summarized in Table 3. They can be classified into three groups according to the chemical forms of the frameworks: (**1**) with Na–Sb–O–S, (**2**) and (**3**) with K–Sb–O–S, and (**4**) and (**5**) with Na–Sb–O–Se. Some influence of the substitutions of Na with K, or S with Se on the structures can be observed in the

Table 3. Crystallographic Data and Mean Interatomic Distances and Bond Angles of $A_3Sb_7O_9(S,Se)_3 \cdot X$ Series Compounds

	(1)	**(2)**	**(3)**	**(4)**	**(5)**
Compound	$Na_3Sb_7O_9S_3 \cdot X$	$K_3Sb_7O_9S_3 \cdot X$	$K_3Sb_7O_9S_3 \cdot X$	$K_3Sb_7O_9Se_3 \cdot X$	$K_3Sb_7O_9Se_3 \cdot X$
X site	(Na, □)Ow_6-octahedron	Zeolitic water	(Na, □)Ow_6-octahedron	$SbOw_3$-pyramid	(□, Sb)Ow_6-octahedron
S. G.	$P6_3$	$P6_3$	$P6_3$	$P6_3$	$P6_3$
a(Å)	14.152(3)	14.256±0.005	14.2513(3)	14.40(1)	14.422(4)
c(Å)	5.5758(7)	5.621±0.002	5.5900(1)	5.568(2)	5.448(8)
Sb–O (Å)	1.972	1.98	1.979	1.98	1.97
Sb–S (Å)	2.295	2.36	2.304	—	—
Sb–Se (Å)	—	—	—	2.481	2.459
Na–O (Å)	2.76	—	—	2.75	2.75
K–O (Å)	—	2.87	2.84	—	—
Na–S (Å)	2.899	—	—	—	—
Na–Se (Å)	—	—	—	2.99	3.022
K–S (Å)	—	3.24	3.168	—	—
X–Ow (Å)	2.24	—	2.25	2.05	2.20
O–Sb–O (°)	88.2	89	88.8	88.6	88.0
S–Sb–S (°)	110.5	105.8	111.1	—	—
Se–Sb–Se (°)	—	—	—	106.1	107.1

(1): Sabelli et al.[2] **(2)**: Graf and Schäfer.[1] **(3)**: Sabelli et al.[2] **(4)**: Kluger and Pertlik.[4] **(5)**: present study.

data listed in Table 3. The differences among the Sb–O distances are negligivle, as mentioned by Sabelli et al.[2] The difference in the O–Sb–O angles among these structures was also negligible. These results suggest that the size of the tunnel structure is not affected by the substitutions of the K atom for the Na atom and that of the S atom for the Se atom. Therefore, the lengths of the c-axis, which is defined only by the crystallographic repetition period of the tunnel structure, are practically equal to each other.

The substitution of Na atom with K atom directly affects the interatomic distances between the alkaline atoms and the oxygen atoms of the Sb–O tunnel structure. The distances between the K atoms and the 6_3 axes running at the center of the tunnel frameworks (3.50 Å for (**2**), and 3.52 Å for (**3**)) are shorter than those between Na atoms and the 6_3 axes (3.72 Å for (**1**), 3.71 Å for (**4**), and 3.69 Å for (**5**)). These values indicate that the larger K atom is located away from the wall of the tunnel framework, and is close to the center of the tunnel.

The (Na,K)–(S,Se) bondings are almost perpendicular to the c-axes. The interatomic distances of these bondings are remarkably influenced by the substitutions. Among these distances, the K–S distances is the longest, and the Na–S distance is the shortest. However, the lengths of the a-axes for $K_3Sb_7O_9S_3 \cdot X$, (**2**) and (**3**), are shorter than those for $Na_3Sb_7O_9Se_3 \cdot X$, (**4**) and (**5**). This can be interpreted by that the shift of the K atoms towards the center of the tunnel, which is significant enough to compensate for the effect of the longest K–S distance on the length of the a-axis.

On the other hand, the substitution of larger Se for smaller S extends the space between the tunnel structures to make the a-axis longer. This substitution affects the a-axis length more than that of the K atom for the Na atom.

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