

Synthesis and Crystal Structure of a New Quaternary Thioantimonate, Na₉Gd₅Sb₈S₂₆

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The first Na-containing quaternary rare-earth thioantimonate, Na₉Gd₅Sb₈S₂₆, was synthesized from the reaction of Gd metal, Sb, and S in Na₂S flux at 750°C. Black plate-shaped crystals were obtained and their crystal structure was determined by the single-crystal X-ray diffraction method. This compound crystallizes in the orthorhombic space group *Pnma* (No. 62) with a unit cell of $a = 11.406(3)$ Å, $b = 23.765(2)$ Å, $c = 16.923(5)$ Å, and $Z = 4$. Na₉Gd₅Sb₈S₂₆ has a complex three-dimensional structure that consists of SbS₃, SbS₄, GdS₆, and GdS₇ units. In the structure, three crystallographically different Gd atoms form a staircase-shaped building block, where two Gd atoms share disulfide ions, S₂²⁻. The formula of the compound can be described as (Na⁺)₉(Gd³⁺)₅(Sb³⁺)₈(S²⁻)₂₂(S₂²⁻)₂. Measurement of the optically diffuse reflectance indicates that Na₉Gd₅Sb₈S₂₆ is a semiconductor with a band gap of 1.63 eV. © 2001 Academic Press.

Key Words: Na₉Gd₅Sb₈S₂₆; crystal structure; band gap; disulfide ion; thioantimonate.

1. INTRODUCTION

Recently, group 15 chalcogenides have been actively explored because of their structural diversities and potential thermoelectric applications (1). Many ternary chalcocantimonates of alkaline or alkaline earth (2), main group metals (3), and transition metals (4) with various structures have been synthesized. Rich structural variations in these compounds are derived from the stereochemically active Sb lone pair electrons (5) Along with the coordinate character of Sb, it is expected that the addition of large electropositive cations such as lanthanides into [Sb_xQ_y]ⁿ⁻ building blocks leads to new compounds with more complex structure. Especially, rare-earth elements may cause unique metal-chalcogen bonding characters due to their large size and high coordination numbers. This strategy also has been applied to synthesize novel multinary chalcocantimonates and some of the ternary rare-earth antimony chalcogenides have been reported (6).

However, rare-earth quaternary phases in this class are quite limited. Reported rare-earth chalcocantimonates are K₂(RE)_{2-x}Sb_{4+x}Se₁₂ (RE = La, Ce, Pr, Gd) (7) AU₂SbQ₈ (A = K, Rb; Q = S, Se) (8) KThSb₂Se₆ (9) K₂Gd₂Sb₂Se₉ (10), and K₂La₂Sb₂S₉ (10) and known quaternary Bi compounds are BaLaBi₂S₆ (9) and ALn_{1+x}Bi_{4+x}S₈ (A = K, Rb; Ln = La, Ce, Pr, Nd) (11) Here we report the synthesis and the structure of a new quaternary rare-earth thioantimonate, Na₉Gd₅Sb₈S₂₆.

2. EXPERIMENTAL SECTION

Synthesis. Na₉Gd₅Sb₈S₂₆ was prepared from the mixtures of 1.36 mmol of Na₂S (99% Kojundo), 1.16 mmol of Gd chips (99.9% Aldrich), 4.55 mmol of Sb powder (99.999% Kojundo), and 11.38 mmol of S (99.998% Aldrich). The reacting mixture was loaded in a quartz tube and then doubly sealed under high vacuum. The mixture was heated slowly up to 750°C, kept for 6 days, and cooled to room temperature by lowering 5°C/hr. A few air- and water-stable black square plate crystals were obtained along with Sb₂S₃. The existence of four elements was confirmed qualitatively by an energy-dispersive X-ray (EDX) spectrometer equipped with an electron probe microanalysis (EPMA, JXA-9600, EDX, LinkeXL).

Once the stoichiometry of the Na₉Gd₅Sb₈S₂₆ was determined from the single-crystal X-ray structure analysis, Na₉Gd₅Sb₈S₂₆ was prepared rationally as a single phase starting from the exact stoichiometry of Gd, Sb₂S₃, S, and excess Na₂S flux in an evacuated quartz tube. The product was washed with DMF, ethanol, and distilled water several times to remove the flux. No other X-ray diffraction peaks of binaries and ternaries are observed in the X-ray diffraction pattern of the rationally synthesized sample. Under the microscope the product was homogeneous in color and crystal shape. After the separation of the product, the yield was about 70%.

X-ray crystallography. Data were collected from a single crystal with dimensions of 0.20 × 0.18 × 0.16 mm

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TABLE 1
Crystallographic Data for Na₉Gd₅Sb₈S₂₆

Formula weight	2800.72
Temperature (K)	150(2)
Wavelength ($\lambda = K\alpha$, Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pnma</i> (No.62)
Unit cell dimensions (Å)	$a = 11.406(3)$ $b = 23.765(2)$ $c = 16.923(5)$
Volume (Å ³)	4587.4(19)
Z	4
Calculated density (g/cm ³)	4.055
Absorption coefficient (mm ⁻¹)	13.021
Θ range for data collection (deg)	2.75 to 30.02
Goodness-of-fit on F^2	1.007
Data/restraints/parameters	6798/0/231
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] ^a	$R1 = 0.0444$, $wR2 = 0.1092$
R indices ($F_o^2 > 0$)	$R1 = 0.0692$, $wR2 = 0.1209$
Largest diff. peak and hole (eÅ ⁻³)	2.576 and -4.202

$$^a R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|; \quad wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}; \\ w = \sigma_F^{-2}.$$

on a Nonius Kappa-CCD diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) (12). The CCD data were integrated and scaled using the DENZO-SMN software packages (13). The absorption correction was carried out by semiempirical methods using equivalent reflections using the DENZO-SMN software package. The initial positions of all atoms were obtained from direct methods and the structure was refined by full-matrix least-squares techniques with the SHELX-97 program (14). The observed Laue symmetry and systematic extinction suggested the space groups *Pna2*₁ and *Pnma*. Subsequent refinements confirmed the centrosymmetric space group *Pnma*. The final cycle of refinement performed on F_o^2 with 6798 unique reflection converged to residuals $wR2(F_o^2 > 0) = 0.1209$ and the conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.0444 (15). The complete data collection parameters and details of structure solution and refinement results are given in Table 1. Final atomic positions and displacement parameters are given in Table 2. Selected bond lengths and angles are also shown in Table 3.

Solid-state UV/vis spectroscopy. Measurements of optical diffuse reflectance were performed at room temperature with a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. BaSO₄ was used as a 100% reflectance standard. Samples were prepared by grinding them to a fine powder and spreading them on the compacted surface of the standard material preloaded into a sample holder. The reflectances vs wavelength data were converted to absorption data through the Kubelka–Munk function (16).

3. RESULTS AND DISCUSSION

Na₉Gd₅Sb₈S₂₆ is a new Na-containing quaternary rare-earth thioantimonate. Figure 1 is the projection along the a -axis of Na₉Gd₅Sb₈S₂₆, where Na–S bonds are not indicated for clarity. This compound has a three-dimensional character with cross-shaped tunnels running along the a -axis. The three-dimensional framework is made up of condensed SbS₆, GdS₆, and GdS₇ polyhedra units and columns condensed by like polyhedra are aligned in parallel fashion along the b -axis direction as shown in Fig. 1. Three Gd-centered polyhedra condensed in three columns are aligned side by side in the order of GdS₇/GdS₆/GdS₇ and Sb-centered polyhedra are condensed in two columns, forming tunnels in between. Na atoms are widely distributed with geometry similar to that of Gd atoms except the columns are filled with Sb atoms.

Figure 2 is a projection along the b -axis where disulfide ligands around Gd(1) and Gd(2) atoms are clearly shown. S(10)–S(14) and S(11)–S(13) dimers attached on Gd(1) and Gd(2) are facing each other and connected by two SbS₄

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for Na₉Gd₅Sb₈S₂₆

Atoms	x	y	z	$U(\text{eq})^a$
Gd(1)	9882(1)	3311(1)	1272(1)	7(1)
Gd(2)	4958(1)	3308(1)	8731(1)	7(1)
Gd(3)	2417(1)	2500	1(1)	8(1)
Sb(1)	2604(1)	4094(1)	9963(1)	8(1)
Sb(2)	2329(1)	4213(1)	7404(1)	9(1)
Sb(3)	7611(1)	4143(1)	47(1)	8(1)
Sb(4)	7609(1)	4229(1)	2465(1)	8(1)
S(1)	9755(2)	4125(1)	2473(1)	9(1)
S(2)	9819(2)	5873(1)	2546(1)	9(1)
S(3)	7553(1)	4996(1)	3565(1)	8(1)
S(4)	7547(1)	5019(1)	1496(1)	9(1)
S(5)	2389(1)	3401(1)	1049(1)	10(1)
S(6)	7460(1)	3444(1)	1109(1)	9(1)
S(7)	7382(1)	3459(1)	8967(1)	10(1)
S(8)	9998(2)	2500	84(2)	8(1)
S(9)	4828(2)	2500	9922(1)	9(1)
S(10)	4187(2)	2500	7616(1)	13(1)
S(11)	841(2)	2500	2307(1)	14(1)
S(12)	2468(2)	3376(1)	8901(1)	10(1)
S(13)	8988(2)	2500	2303(1)	14(1)
S(14)	6030(2)	2500	7782(1)	12(1)
S(15)	9768(1)	4144(1)	59(1)	9(1)
S(16)	4745(1)	4136(1)	9941(1)	10(1)
Na(1)	4882(2)	3311(1)	6267(2)	11(1)
Na(2)	4951(2)	3302(1)	1278(2)	10(1)
Na(3)	26(2)	5028(2)	1232(2)	14(1)
Na(4)	4944(2)	5030(2)	8773(2)	13(1)
Na(5)	7416(3)	2500	17(2)	4(1)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for Na₉Gd₅Sb₈S₂₆

Bond Distances			
Gd(1)–S(1)	2.8104(18)	Gd(1)–S(5)	2.8926(19)
Gd(1)–S(8)	2.7870(19)	Gd(1)–S(6)	2.7946(18)
Gd(1)–S(11)	2.8246(18)	Gd(1)–S(13)	2.7925(17)
Gd(1)–S(15)	2.8551(18)	Gd(2)–S(2)	2.8062(18)
Gd(2)–S(9)	2.7879(19)	Gd(2)–S(7)	2.8162(18)
Gd(2)–S(10)	2.8326(17)	Gd(2)–S(14)	2.7867(17)
Gd(2)–S(16)	2.8498(18)	Gd(2)–S(12)	2.8589(19)
Gd(3)–S(9)	2.752(3)	Gd(3)–S(8)	2.764(2)
Gd(3)–S(5) × 2	2.7800(18)	Gd(3)–S(12) × 2	2.7924(18)
Sb(1)–S(16)	2.4443(19)	Sb(1)–S(12)	2.4835(18)
Sb(1)–S(5)	2.4788(18)	Sb(2)–S(2)	2.4599(19), 3.268(2)
Sb(2)–S(4)	2.6117(17)	Sb(2)–S(7)	2.9315(18)
Sb(2)–S(3)	2.4987(17)	Sb(3)–S(15)	2.4602(19)
Sb(3)–S(6)	2.4538(18)	Sb(3)–S(7)	2.4601(18)
Sb(3)–Sb(16)	3.274(2)		
Sb(4)–S(1)	2.459(2), 3.267(2)	Sb(4)–S(3)	2.6056(17)
Sb(4)–S(4)	2.4940(17)	Sb(4)–S(6)	2.963(2)
Na(1)–S(12)	2.968(3)	Na(1)–S(14)	3.469(3)
Na(2)–S(1)	2.890(3)	Na(2)–S(13)	3.256(4)
Na(3)–S(15)	2.950(4)	Na(4)–S(3)	2.878(3)
Na(4)–S(16)	2.964(4)	Na(5)–S(7)	2.889(3)
S(10)–S(14)	2.121(4)	S(11)–S(13)	2.114(4)
Bond Angles			
S(13)–Gd(1)–S(6)	77.22(6)	S(8)–Gd(1)–S(1)	179.70(6)
S(13)–Gd(1)–S(11)	44.20(7)	S(15)–Gd(1)–S(5)	84.25(5)
S(9)–Gd(2)–S(2)	177.79(6)	S(14)–Gd(2)–S(10)	44.35(7)
S(7)–Gd(2)–S(16)	83.95(5)	S(10)–Gd(2)–S(12)	78.26(6)
S(9)–Gd(3)–S(5)	92.45(5)	S(8)–Gd(3)–S(12)	93.13(5)
S(5)–Gd(3)–S(12)	177.75(5)		
S(5)–Sb(1)–S(12)	94.22(6)	S(4)–Sb(1)–S(3)	98.73(4)
S(16)–Sb(1)–S(15)	175.10(5)	S(3)–Sb(1)–S(5)	82.52(5)
S(2)–Sb(2)–S(2)	169.64(5)	S(2)–Sb(2)–S(3)	97.95(6), 92.38(5)
S(3)–Sb(2)–S(4)	86.44(6)	S(7)–Sb(2)–S(12)	104.10(5)
S(16)–Sb(3)–S(15)	177.35(5)	S(6)–Sb(3)–S(15)	93.73(6)
S(7)–Sb(3)–S(6)	95.09(6)	S(3)–Sb(3)–S(4)	100.37(4)
S(1)–Sb(4)–S(1)	169.72(5)	S(6)–Sb(4)–S(4)	87.88(5)
S(3)–Sb(4)–S(4)	86.67(6)	S(5)–Sb(4)–S(1)	90.73(5), 81.39(4)

units. Three crystallographically different Gd atoms, Gd(1), Gd(2), and Gd(3), are connected forming a staircase-shaped building block (Fig. 3). There is a mirror plane perpendicular to the *b*-axis passing through Gd(3), S(13), S(11), S(8), S(9), S(10), and S(14). The neighboring staircase blocks are connected to each other through Sb atoms. Gd(1) is coordinated by seven S atoms with average distances of 2.8224(18) Å, forming a distorted pentagonal bipyramid. Two neighboring Gd(1)-centered pentagonal bipyramids share the edge of basal plane, S(13)–S(11), and the axial sulfur atom S(8). The basal pentagonal plane has one (S₂)²⁻ unit forming one short edge of the pentagonal plane. The S(13)–S(11) distance of the (S₂)²⁻ dimer in Gd(1)S₇ is 2.114(4) Å, which is very comparable with the typical S–S bond length of 2.118(5)–2.141(1) Å as observed in

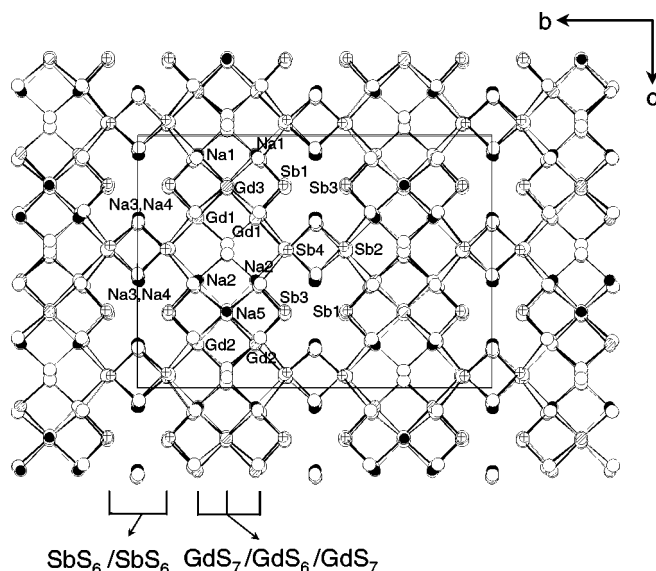


FIG. 1. Crystal structure of Na₉Gd₅Sb₈S₂₆ projected along the *a*-axis. Dashed and open circles are Gd and S atoms, respectively. Crossed and solid filled circles indicate Sb and Na atoms, respectively. S atoms are not labeled for clarity. The unit cell boundary is also shown.

K₂La₂Sb₂S₉ and BaLaBi₂S₆ (9,10). Gd(2) has a local environment similar to those of Gd(1), where the average Gd(2)–S bond distance is 2.8197(18) Å and the S(10)–S(14) distance of the S₂²⁻ unit is 2.121(4) Å. The Gd(1)- and Gd(2)-centered pentagonal bipyramids are connected via the

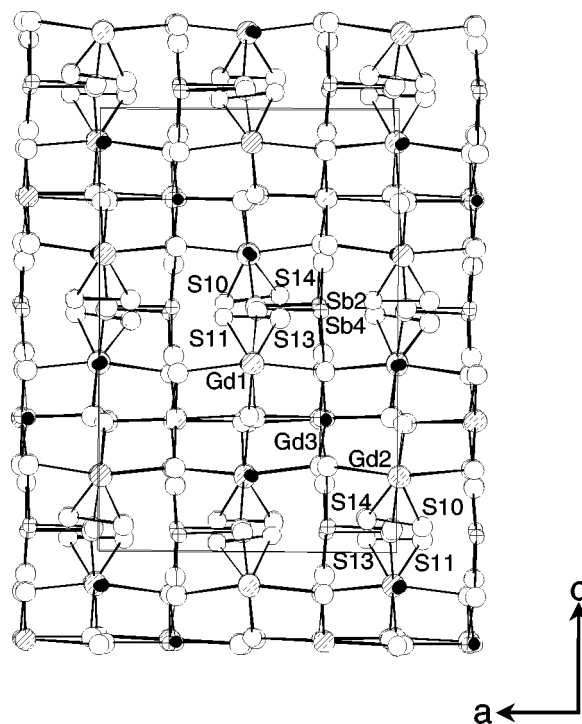


FIG. 2. The projection along the *b*-axis where (S–S)²⁻ bonds around Gd atoms are shown clearly. Na atoms are omitted for clarity.

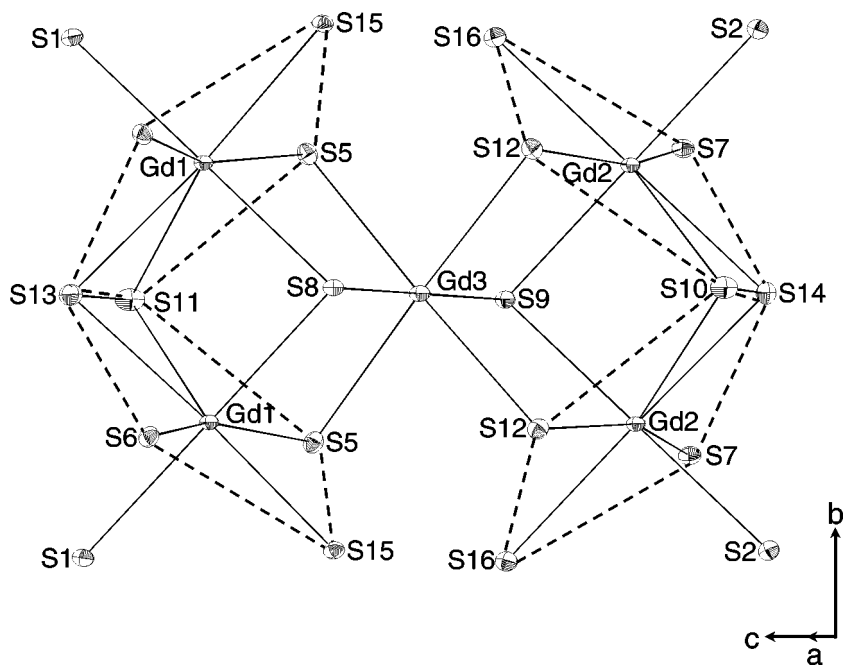


FIG. 3. Thermal ellipsoid (50%) coordinations of Gd(1), Gd(2), and Gd(3) atoms with (S-S) dimers. Basal planes of pentagonal bipyramids are displayed with dashed lines. There is a mirror plane perpendicular to the *b*-axis passing through Gd(3), S(13), S(11), S(8), S(9), S(10), and S(14).

Gd(3)-centered octahedron by sharing their two edges (Fig. 3). The coordination features found in $\text{Na}_9\text{Gd}_5\text{Sb}_8\text{S}_{26}$ —the pentagonal bipyramids and staircase-shaped arrangement—are unique in rare-earth chalcogenides. This compound can be described as $(\text{Na}^+)_9(\text{Gd}^{3+})_5(\text{Sb}^{3+})_8(\text{S}^{2-})_{22}(\text{S}_2^{2-})_2$.

Figure 4 shows a side view of Sb-centered polyhedron. The four crystallographically different Sb atoms in this compound are surrounded by six sulfur atoms with a formal charge of +3. Sb(1) and Sb(3) have three short Sb-S bonds in the range of 2.4443(19)–2.4835(18) Å and three long bonds at 3.218(2)–3.287(2) Å and these Sb-S bond distances

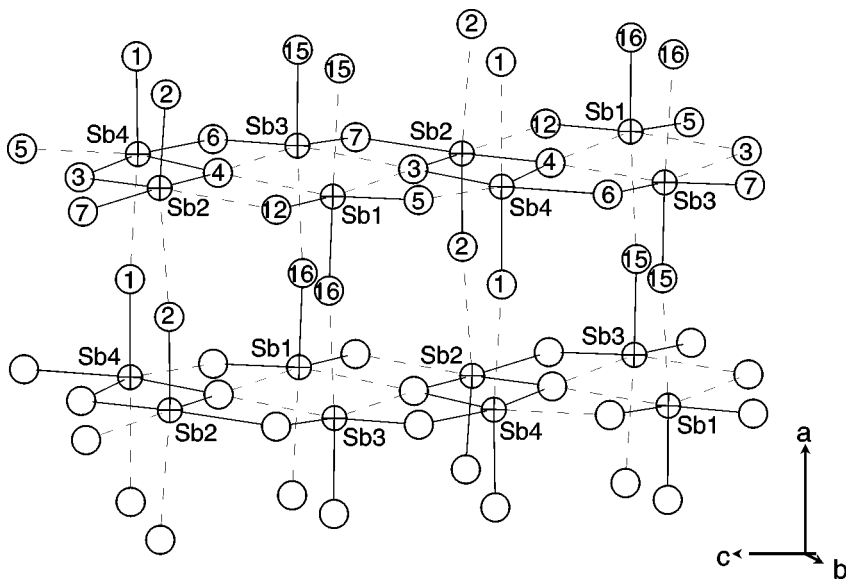


FIG. 4. A side view of Sb-centered polyhedron blocks. Solid lines stand for bonds ranging 2.444(2)–2.932(2) Å and dashed lines are bonds ranging 3.203(2)–3.287(2) Å. Sulfur atoms are labeled with only numbers.

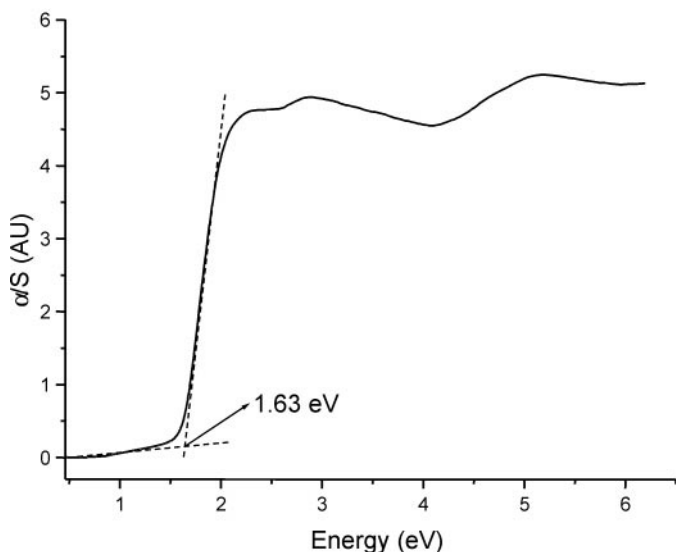


FIG. 5. Optical absorption spectrum of $\text{Na}_9\text{Gd}_5\text{Sb}_8\text{S}_{26}$ with band-gap value.

are comparable to those found in other ternary and quaternary antimony sulfides such as $\text{Cs}_3\text{Sb}_5\text{Sb}_9$ and $\beta\text{-Rb}_2\text{Sb}_4\text{Sb}_7$ (17,18). This type of distorted geometry indicates that the 5s lone pair electrons of Sb are stereochemically active and they are directed toward the three longer Sb–S bonds. Although the longer distances between 3.218(2)–3.287(2) Å are too far to be bonding interactions, they are still shorter than the sum of the Sb–S van der Waals radius, 4.05 Å (19). Therefore, the local coordinations around Sb(1) and Sb(3) can be described as pseudo-octahedral with three weak interactions. Sb(2) and Sb(4) are in the center of a pseudo-octahedron with four shorter Sb–S distances of 2.460(2)–2.9315(18) Å and two longer distances of 3.203(2)–3.268(2) Å. These four crystallographically different Sb-centered octahedra share their basal edges, forming infinite double chains along the *c*-axis which are also found in $\text{K}_2\text{Gd}_2\text{Sb}_2\text{Se}_9$ and $\text{K}_2\text{La}_2\text{Sb}_2\text{S}_9$ (9). The infinite double chains are stacked along the *a*-axis by sharing their apexes to form square-shaped channels.

The local geometries of Na and Gd atoms are similar. Seven S atoms coordinate to the Na(1) and Na(2), respectively, with the same local geometry as the polyhedra of Gd(1)S₇ and Gd(2)S₇. The bond distances of Na(1)–S are in the range of 2.900(3)–3.464(3) Å and those of Na(2)–S are in the range of 2.890(3)–3.256(4) Å. The Na(1)- and Na(2)-centered pentagonal bipyramids are connected through the Na(5)-centered octahedron, forming a staircase geometry as in the Gd-centered polyhedra. The similarity in the ionic radii of Na (1.13–1.26 Å) and Gd (1.078–1.14 Å) (20) rationalizes similar geometry and alternative locations of Na and Gd atoms. The Na(3) and Na(4) atoms form slightly distorted octahedra, sharing their basal edges with the Na–S distance ranging 2.863(3)–3.017(4) Å.

After the separation of pure $\text{Na}_9\text{Gd}_5\text{Sb}_8\text{S}_{26}$ phase from the stoichiometric reaction with excess Na_2S flux, the band-gap of the dark brown powder was measured. Since the compound is valence precise, semiconducting characteristics are expected. The result of optical absorption measurement confirms that this compound is a semiconductor with a band-gap of 1.63 eV (Fig. 5). This compound is air- and moisture-stable.

In summary, we have synthesized a new quaternary phase with three-dimensional structure, where basic building blocks are condensed polyhedra of GdS₇, GdS₆, and SbS₆ and disulfide ligands. The similarity in size of cations Gd and Na and stereochemically active Sb lone pair electrons seems responsible for the new compound with a more unique structure. Continuing studies exploring quaternary chalcogenides with different size of cations may result in interesting unique structures.

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