Synthesis, single-crystal structure, and optical absorption of $Rb_2Th_7Se_{15}$

Lukasz A. Koscielski, Eric A. Pozzi, Richard P. Van Duyne, James A. Ibers *

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston 60208-3113, IL, United States

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ABSTRACT

The compound $Rb_2Th_7Se_{15}$ has been synthesized by the solid-state reaction at 1273 K of Th, Rb_2Se_3, Se, and Ge, and its structure has been determined by single-crystal X-ray diffraction methods. Red crystals of $Rb_2Th_7Se_{15}$ crystallize at 100(2) K with four formula units in a new structure type in the monoclinic space group $C_{2h}^5 - P2_1/c$. The structure is three-dimensional and comprises Rb and Th atoms coordinated by Se atoms to form nine-, eight-, and seven-coordinate polyhedra. Infinite channels that contain Rb atoms are present. Crystals of $Rb_2Th_7Se_{15}$ are red in color; an indirect band gap of 1.83 eV was derived from single-crystal optical measurements.

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1. Introduction

Numerous solid-state compounds containing thorium and the chalcogens are known. Those whose structures have been characterized by single-crystal X-ray diffraction methods include binaries, ternaries, and quaternaries. The simplest of these are the binaries for which the compounds ThS_2 [1], Th_2S_3 [2], Th_2S_5 [3], Th_2Se_5 [4], Th_7S_{12} [5], and Th_7Te_{12} [6] are known. In the ternaries, the following compounds are known: ATh_2Q_6 (A=K, Rb, Cs, Cu; Q=Se, Te) [7–11]; Ba_2ThS_6 [12]; $SrTh_2Se_5$ [11]; $MnThSe_3$ [13]; $ThZQ$ (Z=Ge, P, As, O; Q=S, Se, Te) [14–17]; $Th_{0.81}Mo_6S_8$ [18]; ThP_2S_6 [19]; and $ThTe_2I_2$ [20]. The known quaternaries include $ACuThQ_3$ (A=K, Cs, Tl; Q=S, Se) [21–24]; $Ba_2Cu_2ThS_5$ [25]; $K_2Cu_2ThS_4$ [21]; $K_3Cu_3Th_2S_7$ [21]; $KThSb_2Se_6$ [26]; $A_5ThP_3S_{12}$ (A=K, Rb, Cs) [27]; $A_2ThP_3Q_9$ (A=K, Rb; Q=S, Se) [28,29]; $K_{10}Th_3P_{10}S_{36}$ [27]; $Cs_2Th_2P_2Se_{13}$ [30]; and $Cs_4Th_2P_5Se_{17}$ [28].

The present compound, $Rb_2Th_7Se_{15}$, is the second compound discovered in the Rb/Th/Se system, the first being $RbTh_2Se_6$ [8]. Here we report the synthesis, structural characterization, and optical band gap measurements of $Rb_2Th_7Se_{15}$.

2. Experimental

2.1. Synthesis

Caution! ^{232}Th is an α-emitting radioisotope and as such is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials. Th (MP Biomedicals, 99.1%), Ge (Aldrich, 99.99%), Se (Cerac, 99.999%), and Rb (Cerac, 99+%) were used as received. Rb_2Se_3 was prepared in liquid NH_3 according to a literature procedure [31].

A fused-silica tube was loaded with Th (30 mg, 0.129 mmol), Ge (9.4 mg, 0.129 mmol), Se (10.2 mg, 0.129 mmol), and Rb_2Se_3 (52.7 mg, 0.129 mmol), evacuated to near 10^{-4} Torr, flame sealed, and placed in a computer-controlled furnace. The tube was heated to 1273 K in 24 h, kept at 1273 K for 99 h, cooled to 673 K in 198 h, and then rapidly cooled to 298 K in 4 h. The reaction products included red plates in approximately 5 wt% yield based on Th. Their elemental composition was determined to be Rb:Th:Se in the approximate ratio 9:25:66 on an EDX-equipped Hitachi S-3400 SEM. There was no evidence for the presence of Ge. However, attempts to synthesize the compound without Ge were unsuccessful.

2.2. Structure determination

Single-crystal X-ray diffraction data for $Rb_2Th_7Se_{15}$ were collected with the use of graphite-monochromatized Mo$K\alpha$ radiation (λ=0.71073 Å) at 100 K on a Bruker APEX2 diffractometer [32]. The crystal-to-detector distance was 6 cm. The data collection strategy was optimized with the algorithm COSMO in the program APEX2 [32] as a series of 0.3° scans in φ and ω. The exposure time was 10 s/frame. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2 [32]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [33]. The structure was solved with the direct-methods

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* Corresponding author. Fax: +1 847 491 2976.
E-mail address: ibers@chem.northwestern.edu. (J.A. Ibers).

program SHELXS and refined with the least-squares program SHELXL [34]. The atomic positions were standardized with the program STRUCTURE TIDY [35]. Crystal structure data and refinement details are given in Table 1 and in Supporting Material. Selected metrical details are listed in Table 2.

2.3. Optical absorption measurements

Absorbance spectra of a $Rb_2Th_7Se_{15}$ single crystal were gathered over the range 1.39–3.87 eV (890–320 nm) at 298 K. A crystal was mounted on a glass fiber, affixed to a goniometer head, and positioned at the focus of a $40\times$ extra-long working distance objective. Optical data were acquired using an inverted microscope, as previously described [25]. Collected light was spatially filtered using a 200 µm aperture such that a circular region of diameter 5 µm on the crystal was selectively examined. Spectra were acquired for 7 µs and accumulated 200 times. Absorbance measurements using unpolarized light were performed at multiple locations for verification purposes. Absorbance curves were normalized by the crystal thickness at each location to produce the absorption coefficient α. In addition, spectra were collected with a linear polarizer placed below the light source and rotated from 0° to 360° in 10° increments to probe the polarization dependence of absorption. No optical anisotropy was found.

3. Results and discussion

3.1. Synthesis

The compound $Rb_2Th_7Se_{15}$ was synthesized by the solid-state reaction at 1273 K of Th, Rb_2Se_3, Se, and Ge. The final product did not incorporate any Ge. Subsequent attempts to synthesize the compound without Ge were unsuccessful.

3.2. Structure

Dirubidium heptathorium (IV) pentakaidecaselenide, $Rb_2Th_7Se_{15}$, crystallizes with four formula units in the monoclinic space group $C_{2h}^5 - P2_1/c$ with unit cell parameters $a = 15.2384(5)$, $b = 7.8625(2)$, $c = 21.7614(7)$ Å, $\beta = 90.534(1)°$. All atoms in the asymmetric unit are in general positions. As there are no Se–Se bonds in the structure the formal oxidation states for the charge-balanced compound are Rb^{1+}, Th^{4+}, and Se^{2-}.

The structure (Fig. 1) is three-dimensional and comprises Rb and Th atoms coordinated by Se atoms to form nine-, eight-, and seven-coordinate polyhedra (Table 2). Infinite channels that contain Rb atoms are present. We provide here descriptions of these polyhedra, although such descriptions are somewhat arbitrary, especially as the coordination number increases. Atom Rb1 is nine-coordinate and forms a tricapped trigonal prism. Atoms Rb2, Th2, Th3, and Th6 are eight-coordinate and form distorted square antiprisms; Th7 is also eight-coordinate but its coordination geometry is not easily classified. Atoms Th1, Th4, and Th5 are

Table 1
Crystal data and structure refinement for $Rb_2Th_7Se_{15}$.

Formula mass (g mol^{-1})	2979.62
Space group	$C_{2h}^5 - P2_1/c$
a (Å)	15.2384(5)
b (Å)	7.8625(2)
c (Å)	21.7614(7)
β (deg)	90.534(1)
V (Å^3)	2607.2(1)
T (K)	100(2)
Z	4
ρ (g cm^{-3})	7.591
λ (Å)	0.71073
μ (mm^{-1})	64.41
$R(F)^a$	0.0317
$R_w(F_o^2)^b$	0.0631

[a] $R(F) = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (0.0167 F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2
Interatomic distances (Å) in $Rb_2Th_7Se_{15}$.

Atom–atom	Coordination	Minimum	Maximum
Rb1–Se	9; tctp	3.2788(7)	3.7876(7)
Rb2–Se	8; sqap	3.2649(7)	3.5548(7)
Th1–Se	7; pbpy	2.8835(5)	3.0130(5)
Th2–Se	8; d, sqap	2.9322(5)	3.1196 (5)
Th3–Se	8, d, sqap	2.9264(5)	3.1241 (5)
Th4–Se	7; mctbpy	2.8556(5)	3.0653(5)
Th5–Se	7; mctbpy	2.8788(5)	3.0661(5)
Th6–Se	8; d, sqap	2.9481(5)	3.1160 (6)
Th7–Se	8; unknown	2.9197 (6)	3.3274(5)

d=distorted, tctp=tricapped trigonal prism, sqap=square antiprism, pbpy=pentagonal bipyramid, mctbpy=monocapped trigonal bipyramid.
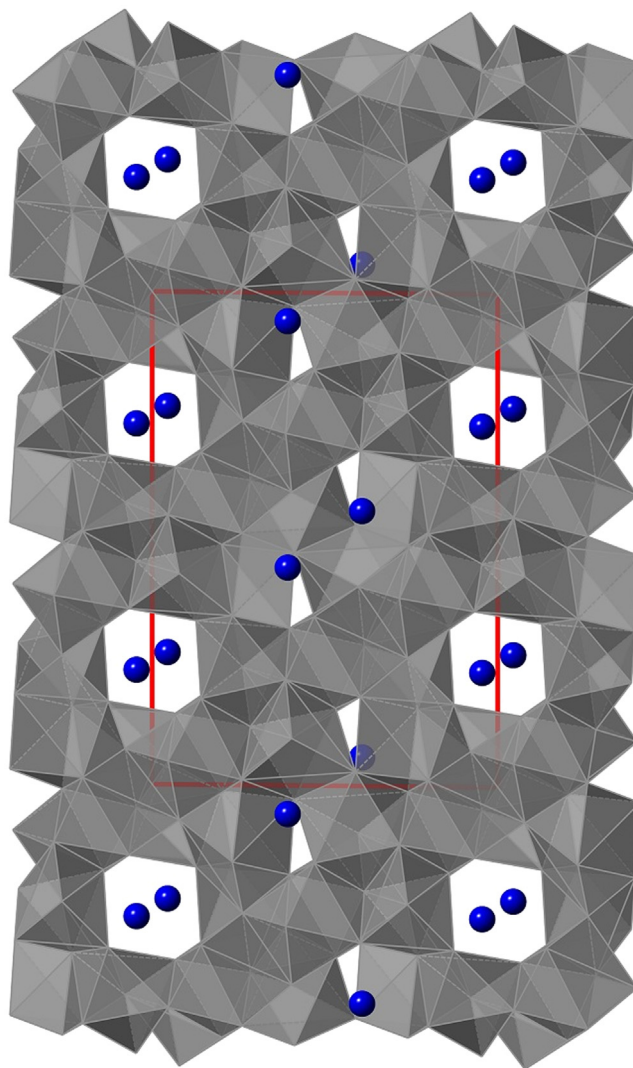

Fig. 1. Structure of $Rb_2Th_7Se_{15}$ viewed down the b-axis. The unit cell is outlined in red. Th−Se polyhedra are gray; Rb atoms are blue. Channels containing Rb are evident. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
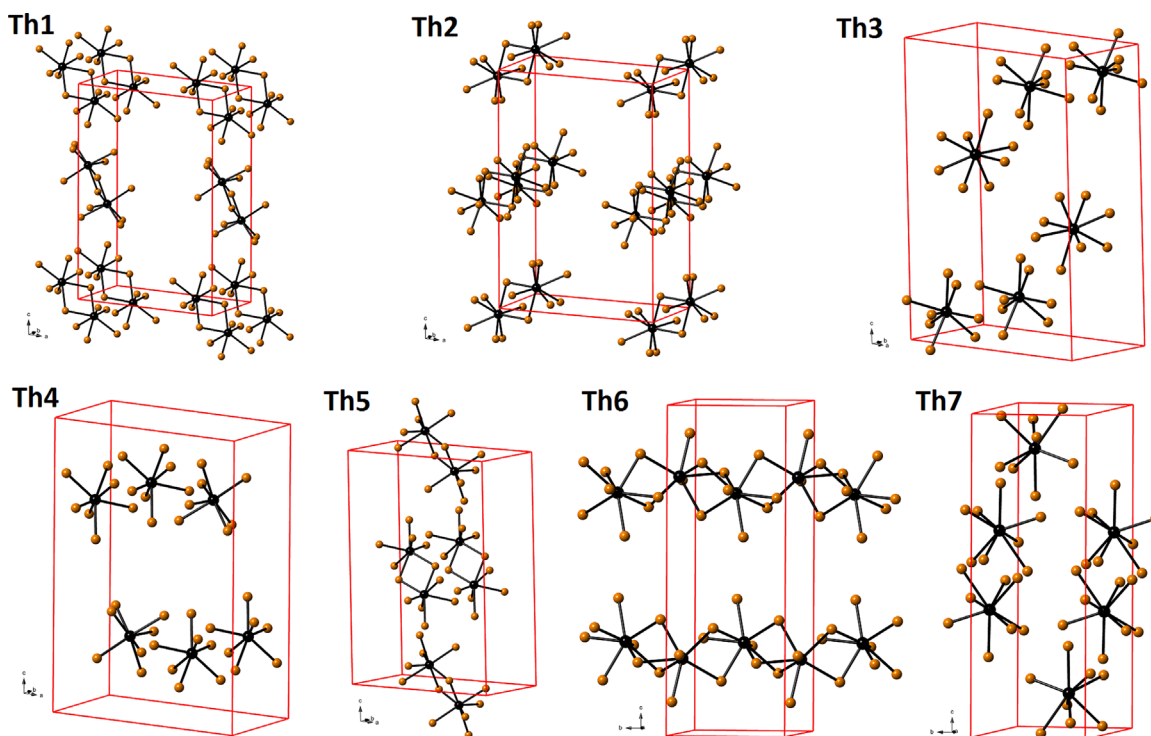
Fig. 2. Coordination environments of the Th atoms in $Rb_2Th_7Se_{15}$. The unit cell is outlined. Key: black—Th; orange—Se. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
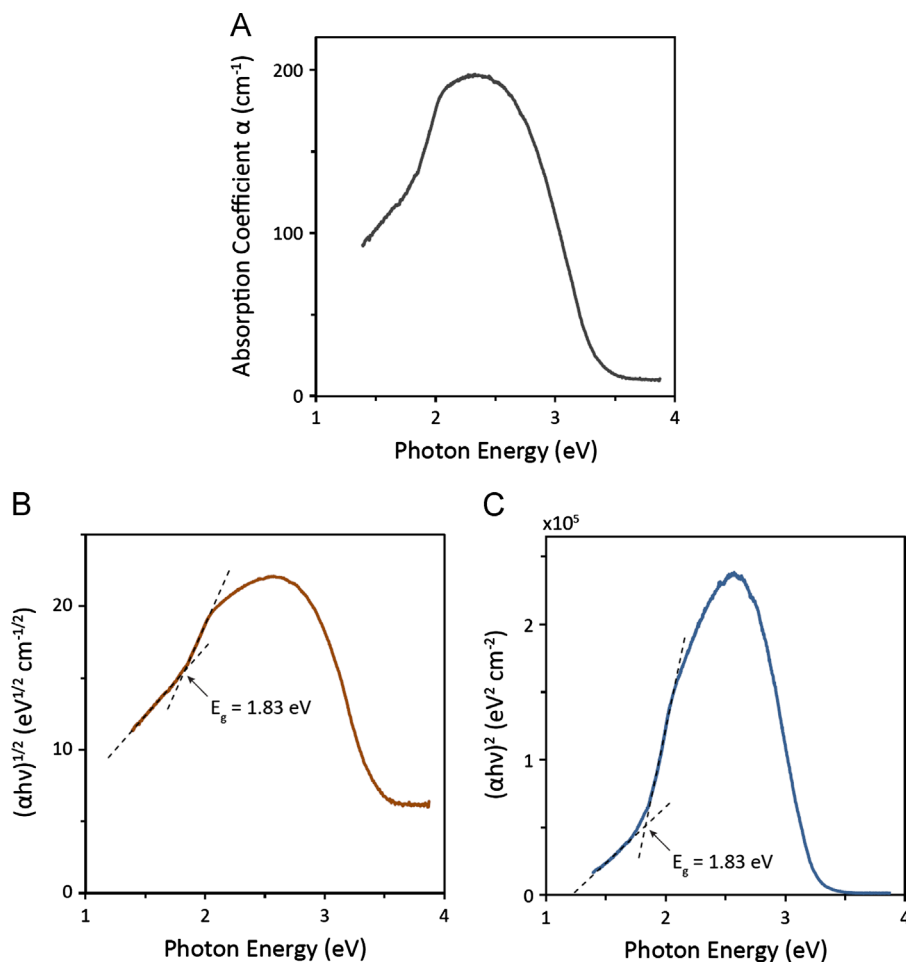

Fig. 3. (A) Absorption spectrum plotted as α vs. $h\nu$ (eV); (B) calculated spectrum for an indirect band gap; and (C) calculated spectrum for a direct band gap.

seven-coordinate: Th1 forms a distorted pentagonal bipyramid and atoms Th4 and Th5 form monocapped trigonal bipyramids.

Fig. 2 displays these various polyhedra and their connectivities. Rb1 polyhedra face-share with each other to form an infinite chain along the *b*-axis; Th6 polyhedra do the same. Rb2 polyhedra edge-share with each other to form discrete pairs throughout the structure; polyhedra of atoms Th1, Th2, and Th5 do the same. The polyhedra of atoms Th3, Th4, and Th7 exist as single units.

$Rb_2Th_7Se_{15}$ is the second compound to be discovered in the Rb/Th/Se system, the first being $RbTh_2Se_6$ [8]. The structure of $Rb_2Th_7Se_{15}$ differs markedly from that of $RbTh_2Se_6$. In that structure there is only one unique Rb and one Th atom, both of which are eight-coordinate; the Rb atom is in a rectangular prism, and the Th atom is in a bicapped trigonal prism, neither of which is present in $Rb_2Th_7Se_{15}$. Additionally, $RbTh_2Se_6$ has a two-dimensional layered structure with Se–Se intermediate bonding, whereas $Rb_2Th_7Se_{15}$ is three-dimensional and has no Se–Se bonding.

Minimum and maximum Rb–Se and Th–Se interatomic distances for each polyhedral arrangement in $Rb_2Th_7Se_{15}$ are listed in Table 2. The Rb–Se distances vary between 3.2649(7) and 3.7876(7) Å and may be compared with Rb–Se distance of 3.499(2) Å in $RbTh_2Se_6$. The Th–Se distances in $Rb_2Th_7Se_{15}$ vary between 2.8835(5) and 3.3274(5) Å, whereas these distances in $RbTh_2Se_6$ vary between 2.965(2) and 3.014(1) Å.

3.3. Optical band gap

The electronic band gap of $Rb_2Th_7Se_{15}$ was characterized through analysis of the fundamental absorption edge observed in the single-crystal absorbance spectrum. Depicted in Fig. 3, the absorption coefficient α was plotted vs. incident photon energy $h\nu$ and compared it with plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs. $h\nu$ to determine whether the band gap is direct or indirect [36]. The superior linear fit to the band edge of the $(\alpha h\nu)^{1/2}$ plot in relation to the band edge of the $(\alpha h\nu)^2$ plot suggests that the band gap of 1.83 eV is indirect [25,37]. This value is consistent with the red color of the compound.

4. Conclusions

Red plates of $Rb_2Th_7Se_{15}$ were prepared from a reaction of Th, Ge, Se, and Rb_2Se_3 at 1273 K. The compound crystallizes in the space group $P2_1/c$ of the monoclinic system in a new structure type that comprises a three-dimensional network of nine-, eight-, and seven-coordinate polyhedra. There are no Se–Se bonds in the structure so charge balance is achieved with $Rb^{1+}Th^{4+}Se^{2-}$. Absorption data indicate that $Rb_2Th_7Se_{15}$ has an indirect optical transition at 1.83 eV.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2013.06.013.

The crystallographic data in cif format for $Rb_2Th_7Se_{15}$ have been deposited with FIZ Karlsruhe as CSD number 426092. These data may be obtained free of charge by contacting FIZ Karlsruhe at +497247808666 (fax) or crysdata@fiz-karlsruhe.de (email).

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