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Electrical and Optical Properties of Cetineite-Type Rb-, Sr-, and Ba-Oxoselenoantimonates(III)

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Large single-crystals of the cetineite-type phases (Rb;Se), (Sr;Se) and (Ba;Se) have been synthesized by hydrothermal reactions and single-crystal X-ray analyses with atomic resolution together with the electrical and optical measurements confirm a trend in the optical gap related to the chemical composition.

Cetineites are crystalline semiconducting oxoselenoantimonates(III) with a zeolite-like channel structure. The name-giving mineral *Cetineite* was described first in 1987 by Sabelli and Vezzalini, who found it in the mine *Le Cetine* in the Tuscany, Italy.[1] Even before the natural (secondary) mineral was found, Graf and Schäfer described a synthetic analog in 1975.[2] Their diffraction data, however, did not reveal the presence of channel-filling guests. Since that time several analogs have been synthesized,[3] and the group of microporous semiconductors has meanwhile even been expanded, e.g. by Palmqvist el al. who most recently introduced a new group of antimony(III) oxide tellurides.[4]

Ten years ago we introduced a synthetic cetineite with the composition $K_6[Sb_{12}O_{18}][SbSe_3]_2{\cdot}6H_2O$ as the first crystalline microporous material with a photo-semiconducting host structure and a bandgap in the visible range.[5] This work was followed by experimental and theoretical studies on the conduction properties and the electronic structure.[6] Most recently we have shown that the aforementioned compound can take up noble gases into the channel structure which may cause reversible changes of the electronic conductivity, while the host lattice retains its structural and compositional integrity and high symmetry.[7] This is a very unique finding encouraging us to investigate this class of materials even further to finally gain an in-depth understanding of the physical properties and to evaluate its potential for technical applications.

The general composition of cetineites is $A_6[Sb_{12}O_{18}][SbX_3]_2{\cdot}(6\text{-mx-y})H_2O{\cdot}x(B^{m+}(OH)m){\cdot}yD$ with A = Na^+, K^+, Rb^+, Ba^{2+}, Sr^{2+}; X = S^{2-}, Se^{2-}; B^{m+} = Na^+, Sb^{3+}; D may stand for an unoccupied lattice site or for further guests. A short-hand notation **(A;X)** is commonly used as, for example, **(K;Se)** for $\mathbf{K}_6[Sb_{12}O_{18}][Sb\mathbf{Se}_3]_2$. As shown in Figure 1, the structure contains one-dimensional $[Sb_{12}O_{18}]$ tubes with a diameter of ca. 0.7 nm, consisting of pyramidal $[SbO_3]$ subunits, which are linked via common oxygen atoms. Separate $[SbX_3]^{3-}$ pyramids are located between the tubes. The channels may be filled by different guest species, e.g. by water molecules or water-coordinated ions, as illustrated in Figure 1.

The electroneutral tubes are held together by predominantly ionic bonds between alkali or earth alkali ions, respectively, lining the inner walls of the tubes and the chalcogen atoms of the separate $[SbX_3]^{3-}$ pyramids. If the alkali cations within the tubes are replaced by divalent cations, replacement of H_2O by OH^- maintains charge balance. Progress in the synthetic method yields the preparation of single crystals up to a length of 2 mm and a hexagonal cross section of 3×10^{-2} mm^2. This has enabled photoemission, optical absorption, and conductivity measurements on the cetineites with compositions (Na;Se), (K;Se), (Na,S) and (K;S).[6a,6c]

In this work we describe the synthesis of single crystals of the cetineite-type phases (Rb;Se), (Sr;Se) and (Ba;Se) large enough for direct electrical addressing. Together with the structural characterization using X-ray single-crystal diffraction we present their optical and conducting properties in comparison to the known related phases (Na;Se) and (K;Se), which could be synthesized with sufficient size and were analyzed before.[6b,6c] Hence, the present work is a continuation of our previous ones expanding the knowledge about structure-property relations of this class of materials.

The individual cetineite phases have been synthesised under hydrothermal conditions. In the typical synthesis the solid starting compounds, elemental Sb and elemental Se, were directly mixed with alkali/alkaline-earth carbonate, hydroxide or selenide, respectively, and water. To all reaction mixtures LiOH was added in order to increase the basicity. Unlike the synthesis of (Na;Se) and (K;Se) templates did not need to be added. After stirring, the mixtures were sealed in Teflon tubes (inner volume 25 mL) in air and then

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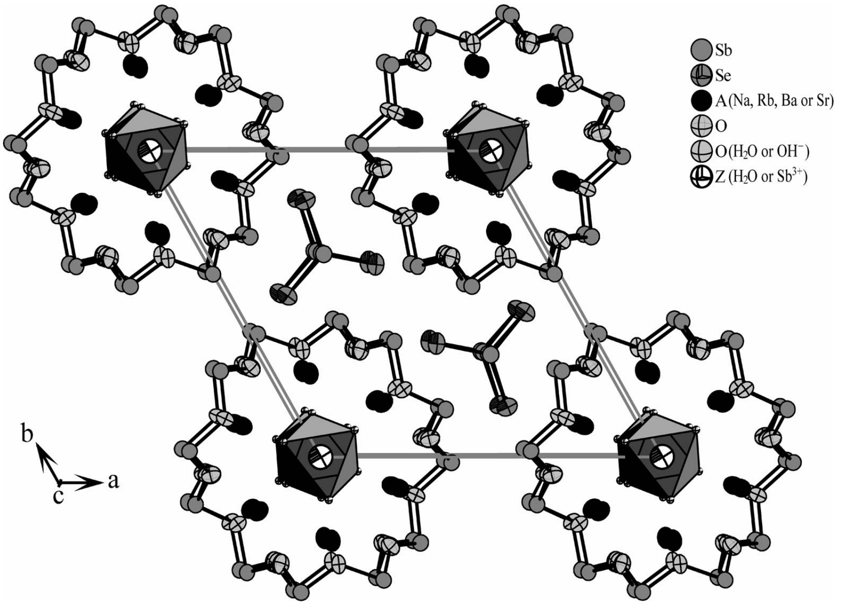

Figure 1. Projection of the structure of (A;Se, A = Na, K, Rb, Sr, Ba) along the [001] axis: Z = H_2O or Sb^{3+}. Displacement ellipsoids are drawn at the 90% probability level.

heated to temperatures between 200 and 220 °C under autogenous pressures for four days. The products were washed with water, filtered and dried in air. For the synthesis of (Rb;Se) and (Sr;Se) we followed the route described by Wang and Liebau.[3] In the case of (Ba;Se) we used BaSe instead of the respective carbonate as a source for the barium cation, leading to a stable reaction product. When $BaCO_3$ was used, the crystals thus obtained became amorphous in air very rapidly, so that no X-ray crystal-structure analysis could be performed.

Similar to (Na;Se) and (K;Se) the (Rb;Se) crystals were found to be of columnar habit, elongated along the hexagonal [001] axis with a maximum length of 0.8 mm. In contrast, the crystals obtained from the syntheses with the divalent cations exhibit a shape of hexagonal dipyramids (cross section of 0.02 mm^2). Independent of their morphology, single crystals of the three cetineite phases have a red to dark-red colour.

The structural analyses of our compounds confirmed, in many cases, the previous results obtained by Wang and Liebau,[3b] but also show some small discrepancies. The crystal structures were solved by means of direct methods[8] in space group $P6_3/m$ (No. 176) and refined by full-matrix least-squares refinement (based on F^2)[9] using anisotropic displacement parameters for all atoms. No effort was made to locate hydrogen atoms due to the high number of heavy atoms in the unit cell. In the structure of (K;Se) the central parts of the tubes are occupied only by water molecules, i.e., by chains of face-sharing octahedral $(H_2O)_6{\cdot}H_2O$ units.[7] In (Na;Se), however, face-sharing octahedral $[(OH^-)_{0.3}\text{-}(H_2O)_{0.7}]_6{\cdot}(Sb^{3+})_{0.6}$ groups are found inside the tubes. The corresponding octahedral positions in the structure of (Rb;Se) were not fully occupied as only small amounts of OH^- and H_2O could be refined, leading to defective $[(OH^-)_{0.1}\text{-}(H_2O)_{0.3}]_6{\cdot}(Sb^{3+})_{0.2}$ octahedra. In (Sr;Se) the $(OH^-)_6$ octahedra found were empty, suggesting the investigation of an effect of gas uptake similar to (K;Se) as described in ref.[7] When (Ba;Se) is synthesized in the presence of $BaCO_3$ as described by Wang and Liebau, the tubes may contain CO_3^{2-} and O^{2-}.[10] In the modified synthesis described here, however, H_2O and OH^- were found within the tubes (see Table 1). The refined compositions, the internal *R* values and the Goodness of fit (GooF) for all synthesized compounds are listed in Table 2.

Optical measurements have been performed under ambient conditions on individual single crystals of each cetineite phase. The UV/Vis spectra were recorded in a range from 400 nm to 800 nm using a Zeiss Axioplan 2 imaging micro-

Table 1. Experimental details for the syntheses.[a]

(Na;Se)[6c]	(K;Se)[6c]	(Rb,Se)	(Sr;Se)	(Ba;Se)
0.39 g Sb 0.37 g Se 0.3 g NaOH 2.23 mL methylamine[b]	0.39 g Sb 0.37 g Se 0.4 g KOH 0.25 mL pentylamine	0.39 g Sb 0.37 g Se 0.82 Rb_2CO_3 0.2 g LiOH	0.19 g Sb 0.37 g Se 0.57g $Sr(OH)_2{\cdot}8H_2O$ 0.3 g LiOH	0.19 g Sb 0.1 g Se 0.2 g BaSe 0.6 g LiOH
4 days, 210 °C	1.3 g H_2O, 4 days, 220 °C	1.3 g H_2O, 4 days, 220 °C	2 g H_2O, 4 days, 210 °C	2 g H_2O, 4 days, 220 °C

[a] Grades: Sb (100 mesh, 99.995%, Aldrich), Se (200 mesh, 99.999%, Alfa Aesar), Rb_2CO_3 (99%, ABCR), LiOH (99.8%, Aldrich), $Sr(OH)_2{\cdot}8H_2O$ (98%, Riedel-de Haën), BaSe (99.5%, Alfa Aesar). [b] 40% in water.

Table 2. Compositions, cell parameters (space group: $P6_3/m$, No. 176), ionic radii of the A-cations, experimental optical energy gap and the specific conductivity of cetineite-phase crystals at room temperature parallel to the crystallographic *c*-axes.[a]

	Composition Refined R values R_1, wR_2 $[I > 2\sigma(I)]$ and Goodness of Fit (GooF)	Cell parameters [nm]	Ionic radius[3b] [pm]	Energy gap [eV]	Specific conductivity [S/m]
(Na;Se)	$Na_6[Sb_{12}O_{18}][SbSe_3]_2[(OH)_{1.8}(H_2O)_{4.2}]\cdot Sb_{0.6}$ $R_1 = 0.023$, $wR_2 = 0.046$, GooF = 1.05	$a = 1.4442(2)$ $c = 0.5561(1)$	98	2.12[6c]	$\sigma_L = 5.4 \times 10^{-7}$ $\sigma_D = 1.42 \times 10^{-8}$
(K;Se)	$K_6[Sb_{12}O_{18}][SbSe_3]_2(H_2O)_6\cdot H_2O$ $R_1 = 0.028$, $wR_2 = 0.063$, GooF = 1.02	$a = 1.4583(2)$ $c = 0.5609(1)$	133	2.03[6c]	$\sigma_L = 1.75 \times 10^{-6}$ $\sigma_D = 1.42 \times 10^{-7}$
(Rb;Se)	$Rb_6[Sb_{12}O_{18}][SbSe_3]_2\ [(OH)_{0.6}(H_2O)_{1.8}]\cdot Sb_{0.2}$ $R_1 = 0.060$, $wR_2 = 0.144$, GooF = 1.03	$a = 1.4715(2)$ $c = 0.5654(1)$	149	1.85	$\sigma_L = 3.26 \times 10^{-6}$ $\sigma_D = 4.52 \times 10^{-7}$
(Sr;Se)	$Sr_6[Sb_{12}O_{18}][SbSe_3]_2(OH)_6$ $R_1 = 0.075$, $wR_2 = 0.201$, GooF = 1.19	$a = 1.4371(5)$ $c = 0.5507(3)$	127	1.94	$\sigma_L = 1.9 \times 10^{-10}$ $\sigma_D = 9.8 \times 10^{-11}$
(Ba;Se)	$Ba_6[Sb_{12}O_{18}][SbSe_3]_2(OH)_6\cdot(H_2O)_{1.4}$ $R_1 = 0.067$, $wR_2 = 0.136$, GooF = 1.22	$a = 1.4513(2)$ $c = 0.5592(1)$	146	1.75	$\sigma_L = 9.5 \times 10^{-11}$ $\sigma_D = 6.5 \times 10^{-11}$

[a] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-418784 (Na;Se), -418785 (Rb;Se), -418786 (Sr;Se), -418787 (Ba;Se).

scope (50-fold magnification) equipped with a UV/Vis diode array detector (J&M) and a Hg lamp as a light source. Absorption spectra of (Rb;Se), (Sr;Se), and (Ba;Se) are shown in Figure 2.

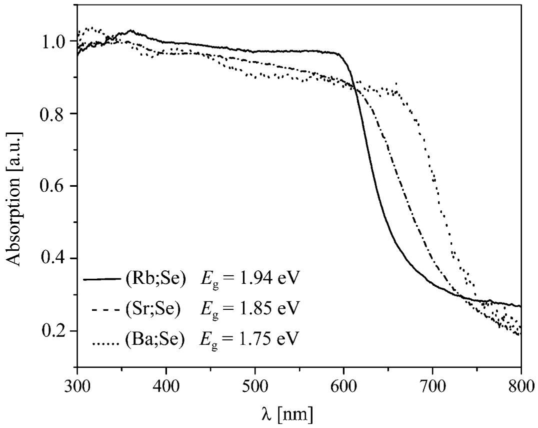

Figure 2. Absorption spectra of (Rb;Se) (solid line), (Sr;Se) (dashed line), and (Ba;Se) (dotted line).

The width of the optical gaps, analyzed by measuring the absorption threshold and determined by using the tangential method, depends on the cetineite's composition. The increasing ionic radius of the A-atom, which leads to an increase of the lattice constants (see Table 2), causes a redshift of the band edge. A similar trend was already observed in mixed phases of (Na, K;S), i.e. the sulfur analogue with varying Na:K ratio.[6a] However, the alkali metal phases revealed a smaller optical gap as referred to the lattice constants and the ionic radii, respectively.

Direct current I was measured using an electrometer (Keithley 6517). The conductance G and resistance R were derived directly from the respective current at a voltage U of 10 V according to Ohm's law. From former impedance and conductivity measurements we know that no significant contact resistances occur, allowing us to perform two-point measurements for the electrical characterization.[5,6] Thus, the I/U characteristics were obtained in the range of –10V to +10V in the dark and under irradiation with white light. The conductivity for (Rb;Se) crystals has been measured parallel and perpendicular to the c axis by applying silver paint contacts as indicated in Figure 3.

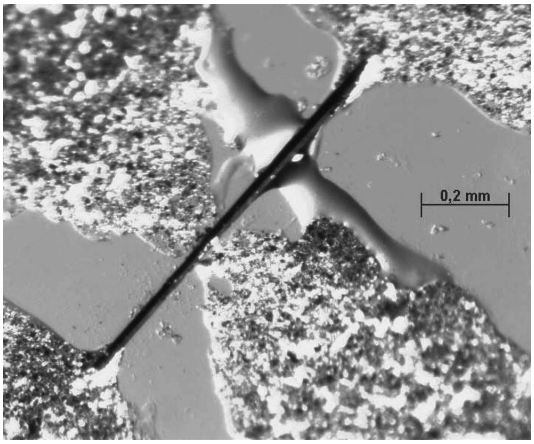

Figure 3. Image of a (Rb;Se) single crystal with electrical contacts (silver paint).

The other crystals were measured only parallel to the c axis because they were too small to allow successful electrical addressing perpendicular to the main crystal axis. These conductance measurements show that all compounds are poor conductors in the dark with an almost linear I/U characteristic. Irradiation with white light causes an increase in conductivity accompanied by a pronounced non-linearity, which is presumably caused by the formation of space charge regions at the shaded electrode areas (Figure 4, a).

The specific conductivity σ of the cetineite crystals parallel to the crystal axes under irradation and in the dark are summarised in Table 2. These values are calculated from the equation $\sigma = (I{*}L)/(U{*}A)$, where L is the length of the respective crystal (unit m) and where A is the square face area (unit m^2). However, the conductivity data scatter over a broad range from 10^{-6} to 10^{-11} [S/m], which may mainly

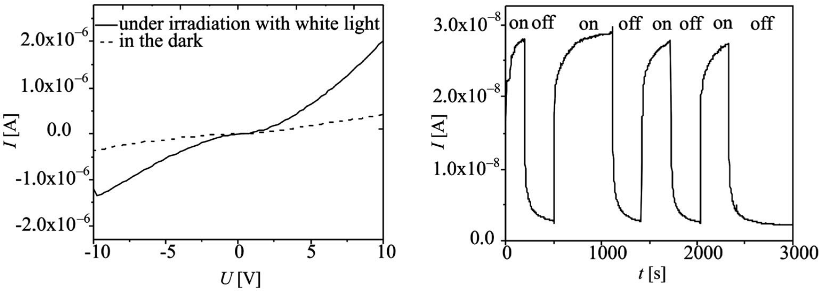

Figure 4. a) I/U curves of a (Rb;Se) single crystal; b) Plot of the current I in the dark and under irradiation with white light showing the relaxation of the excess charge carriers during several switching cycles.

result from crystal defects. As a trend it is found that σ is larger for the phases with alkali metals as compared to those with the earth alkali metals. Measurements of illuminated (σ_L) and non-illuminated (σ_D) crystals show that the conductivity increases under white light by a factor of 38, 12.3, 7.2, 1.9, and 1.5 for (Na;Se), (K;Se), (Rb;Se), (Sr;Se), (Ba;Se), respectively. The specific conductivity of (Rb;Se) measured parallel to the crystallographic $a \times b$ plane was found to be about one order of magnitude smaller than along the c axis. However, the anisotropy of conductivity is smaller as compared to Na;Se.[6c]

To verify whether the optical excitation energy of the photoconductivity corresponds to the optical bandgap, the conductivity for (Rb;Se) has been measured with simultaneous variation of the wavelength of the irradiated light in the range of 400–800 nm. The onset of photoconductivity corresponds to the optical bandgap determined by UV/Vis spectroscopy and gives a value of 1.9 eV. From time-dependent measurements the on/off relaxation time of the photo-excited charge carriers was determined. It was found to be 8.0 s for switching on the white illumination and 9.0 s after switching off. Both time constants are highly reproducible over several switching cycles as shown in part b of Figure 4). Since the intensity of the monochromatic light is low compared to the white light intensity applied for the photoconductivity measurements, the measurements could only be performed on (Rb;Se), and not on the other two compounds due to their lower photoconductivity.

In summary we have shown that the synthesis of large single crystals of the cetineite-type phases (Rb;Se), (Sr;Se) and (Ba;Se) together with the structural, optical and electrical characterization allows comparison to the known related cetineit phases (Na;Se) and (K;Se). We observed a systematic change of the optical bandgap which follows the ionic radii of the cations. Although in a narrow range between 2.12 eV for (Na;Se) and 1.75 eV for (Ba;Se), the optical and photo-conducting properties may be tuned, which provides further insight into structure–property relations of this class of materials, and which may potentially be useful for optical or electronic applications.

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