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Motivation:

Cetineites are oxoselenoantimonates with zeolite-like channel structure, the synthesis of which was described by Wang and Liebau[1)]. In contrast to zeolites and structurally related metal oxides, which are electrical insulators, cetineites have shown to be the first crystalline nanoporous material with a photo-semiconducting host lattice[2)]. This made the material attractive for further detailed experimental and theoretical investigations of the electronic structure of this novel class of nanomaterials.

The general composition of cetineites is:

$A_6(Sb_{12}O_{18})(SbX_3)_2 \cdot (6\text{-}mx\text{-}y)H_2O \cdot x(B^{m+}(OH)_m) \cdot y$

with A = **Na^+, K^+**, Rb^+, Sr^{2+}, Ba^{2+} ;

X = **S^{2-}, Se^{2-}** and B = Na^+, Sb^{3+}, CO_3^{2-}

The phases with A = Na, K and X = S, Se are discussed in this work.

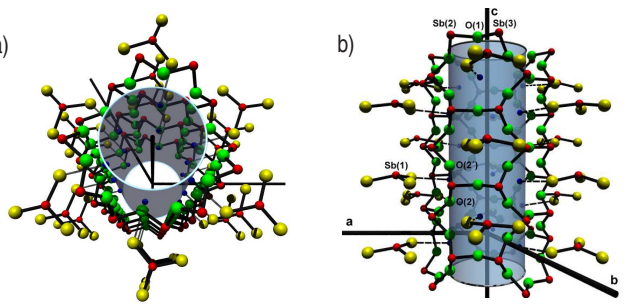

Fig.1: Structure of (Na;Se) in a perspective view into a) and along b) one tube; the channel filling ions (B) are left out in the plot.

Experimental:

Preparation	Hydrothermal reaction of elementary antimony and sulfur or selenium in aqueous NaOH or KOH
Optical Absorption	UV/Vis transmission spectra/Leica MSP-SP.
DC-Conductivity	Keithly Electrometer 6517
AC-Conductivity	EG&G Potentiostat 283 Solartron Gain Phase Analyser SI 1260

Electrical and Optical Properties

The optical excitation energy $E_{Ex,opt}$ has been determined from the plot of $(E_X)^2$ vs. Energy (inset in Fig. 3), which identifies the transition to be direct.

The dc measurements show that all four compounds are poor conductors in the dark with an almost linear characteristic. From irradiation an increase of conductivity results with a distinct nonlinearity at low voltages of approx. ± 1V. This may hint at a Coulomb attraction between the photo generated charge carriers. The linear behaviour above gives no indication of the participation of localized states, e.g., conduction by a hopping process.

Fig. 3 shows the energy resolved photoconductivity. The onset wave length for the four phases corresponds to the respective optical band gap.The values obtained are summarized in Tab. 1.

Impedance measurements in the dark and under irradiation with white light revealed a semicircle in the complex plane, indicating a Debye-like relaxation. The real part of the impedance obtained at the low frequency minimum of the semicircle corresponds to the dc resistance of the crystals. Thus the relaxation may be attributed to an electronic charge carrier relaxation in the volume of the crystals. Ionic conductivity as well as interfacial polarization at the contacts could be excluded.

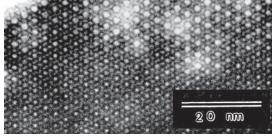

Fig.2: Electron micrograph of the axb plane of (K;Se) showing the channel structure[2)]

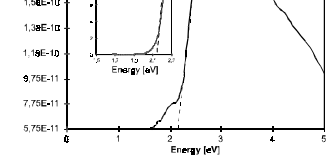

Fig.3: Energy resolved photoconductivity and $(E_x)^2$ vs. Energy (inset) of (Na;Se) along c

Computational:

The numerical computation followed the linear augmented plane wave (LAPW) procedure and yielded density of states (DOS), band structure and dielectric function[3)]. The channel filling ions B^{m+} and water molecules have been discarded in the calculation. We have calculated selfconsistently the potential for the four crystals with 44 atoms per unit cell and an empty sphere centered in the tube.

Bandstructure and Optical Absorption

As a prototype for these compounds the bandstructure of (Na;Se) has been calculated. It displays a stronger dispersion parallel to the c-axis, especially along the Γ-A-direction, and a weaker one perpendicular to it. The binding is stronger along the tubes with main contributions occurring via Sb(2)- (Sb(3)-) oxygen p bonds.

The fundamental gap is framed by states which to a significant degree are made up of Sb d and chalcogen p orbitals of the outer $[SbX_3]^{3-}$ pyramids. They constitute the lateral binding together with the ionic attraction to the cation A^+. The extra charge density accumulated on these pyramids is a candidate for the observed conductivity.The direct gap of slightly more than 0.5 eV occurs at the K-point. The theoretical absorption, represented by the imaginary part of the dielectric function, shows a pronounced maximum if the field points parallel to the tube axes. Its dependence on the chemical composition Fig.4(a) shows the same chemical trend as found in the onset of Im ε above the fundamental gap. This maximum dominates also the extinction coefficient Fig.4(b) which together with a plot of the contributing transistions is displayed in Fig.4(c) for (Na;Se).

Whether the energetic coincidence of this maximum with the onset of photoconductivity bears physical significance will be clarified by calculations of the conductivity which is in progress.

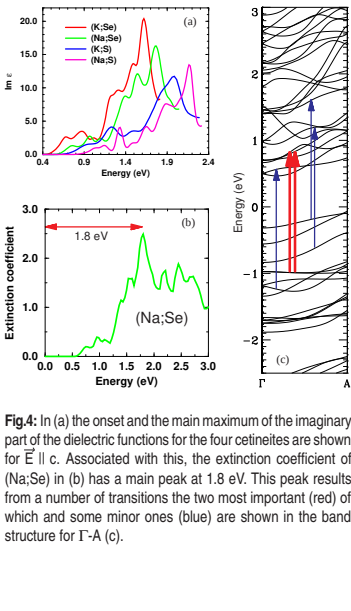

Fig.4: In (a) the onset and the main maximum of the imaginary part of the dielectric functions for the four cetineites are shown for $\vec{E} \parallel c$. Associated with this, the extinction coefficient of (Na;Se) in (b) has a main peak at 1.8 eV. This peak results from a number of transitions the two most important (red) of which and some minor ones (blue) are shown in the band structure for Γ-A (c).

Tab. 1.: Eperimental Band Gap $E_{Ex,opt}$, Energy of Maximum Absorption $E_{Ex,max}$ and Fundamental Gap $E_{G,fund}$ of Cetineites (A;X)

Cetineites(A;X)	$E_{Ex,opt}$ [eV]	$E_{Ex,max}$ [eV]	$E_{G,fund}$ [eV]
(Na;S)	2.38	2.18	0.82
(K;S)	2.29	1.98	0.68
(Na;Se)	2.12	1.77	0.54
(K;Se)	2.03	1.62	0.44

Conclusions:

We have selfconsistently calculated the electronic structure and optical properties of a most promising family of nanoporous compounds. A remarkable difference of more than 1 eV between the calculated fundamental band gap and the calculated pronounced maxima of absorption appears. The latter coincide in energy with the observed onsets of photoconductivity and absorption suggesting that at least the measurements display the pronounced maxima in the frequency dependence of the dielectric function.

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