Cetineites - semiconducting alternative to zeolites ?

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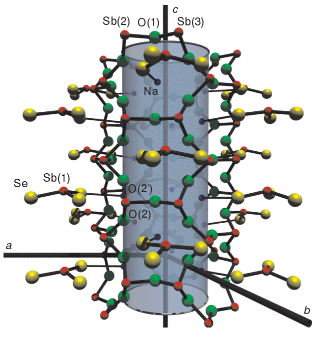
Substance

Cetineites are oxoselenoantimonates with zeolite-like channel structure, the synthesis of which was described by Wang and Liebau[1]. In contrast to the well-known zeolites, which are electrical insulators, cetineites have shown to be the first crystalline nanoporous material with photo-semiconducting host lattice.[2] This was the starting point for detailed experimental and theoretical investigations of the electronic structure of this novel class of nanomaterials. The general composition of cetineites is:

$A_6(Sb_{12}O_{18})(SbX_3)_2{\cdot}(6\text{-}mx\text{-}y)H_2O{\cdot}x(B^{m+}(OH)_m)_y$ with A= Na^+,K^+,Rb^+,Sr^{2+},Ba^{2+}; X=S^{2-},Se^{2-} and B=Na^+,Sb^{3+}, CO_3^{-2}

Cetineite Na;Se



$Na_6[Sb_{12}O_{18}][SbSe_3]_2$

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Methods

Experiment

Dc-conductivity 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. The onset of photoconductivity corresponds to the optical gap determined by UV/Vis microspectrometry[3]. In this work the phases with A=Na^+,K^+ and X=S^{2-},Se^{2-} are discussed. The chemical trend in the optical gaps, ranging from 2.0-2.4eV, which displays a larger gap for Na^+ than for K^+ as well as a larger gap for the S^{2-} compounds in comparison to Se^{2-}. The mixed phase (Na,K;S) displays that the band gap can be tuned by varying the Na:K-ratio. This results give an insight into structure/property-relations in this novel class of nanoporous materials.

Theory

The calculations have been performed with the augmented Fourier components (AFC) version of an extended full potential linearized augmented plane wave (ELAPW) method.[4] The density is separated into two parts: a Fourier part, which represents the charge density of the valence electrons and a narrow MT part, describing the nucleus and the core electron distribution in a spherically symmetric average. The Fourier charge density distribution is easily accessible in this method because the extended LAPW method easily yields the Fourier transform of the valence wave functions, accelerated by the kp-method, because the transfer-matrix is k independent.

The gouging allows to shift density from the MT-part to the fourier-part.

More freedom in the extensions is now possible.

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[2] U. Simon, F. Schüth, S. Schunk, X. Wang, and F. Liebau, Angew. Chem. Intern. Ed. Engl. **36**, 1121 (1997)
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[4] E.E. Krasovskii, F. Starrost and W. Schattke, Phys. Rev. B **59**, 10504 (1999)
[5] F. Starrost, E. E. Krasowskii, W. Schattke, J. Jockel, U. Simon, X. Wang, and F. Liebau, Phys. Rev. Lett. **89**, 3313 (1998)
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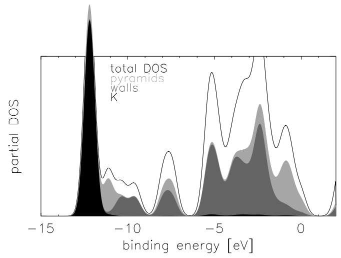
Introduction

We have performed *ab initio* calculations of the energy band structure, dielectric function, and photoelectron energy distribution curves for the (Na;Se) cetineite with various configurations of the guest molecules filling the nanotube.[5] The guest molecules have been found to only slightly affect the optical absorption in the visible and UV photon energy range. At the same time, according to our calculations, their effect must be well seen in the photoemission experiments. The experimentally observed influence of guest molecules on the photoconductivity is apparently caused by changes in the mobility of the carriers rather than by changes in the optical excitation process.

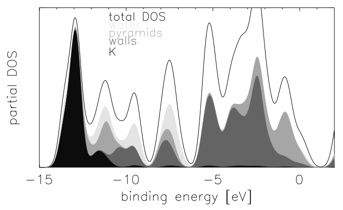
Cetineite Mineral

DOS

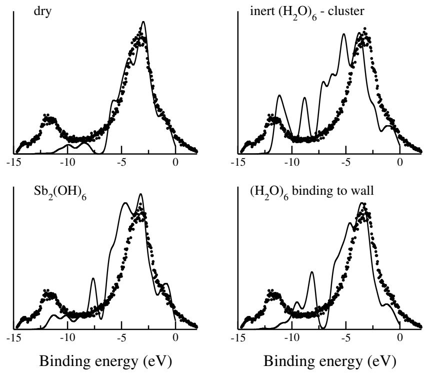


- **Atom-resolved partial DOS** for pure (K;S)
- SbS_3-pyramids (light) - top of valence
- $Sb_{12}O_{18}$ tetrahedra (darker) - wall
- K-atoms (black)
- interstitial (white)
- total DOS (solid line)

- **Atom-resolved partial DOS** for (K;S) + water
- water (very light) - bound to pyramids
- SbS_3-pyramids (light) - top of valence
- $Sb_{12}O_{18}$ tetrahedra (darker) - wall
- K-atoms (black) - split at -12eV
- interstitial (white)
- total DOS (solid line)

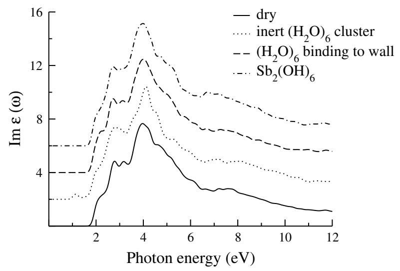


Photoemission



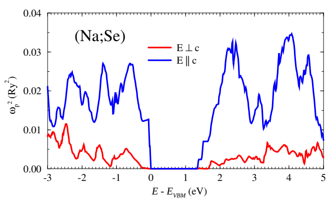
- **angle-integrated UPS** measurement of (Na;Se)+H20 [6] (circles)
- theory: different models for the guests (solid lines)
- significant differents due to the model
- further investigations demanded: PES for dry material
- ... and total-energy-calculation to determine the atomic positions

Optics



- **imaginary part of the dielectric function** of (Na;Se)
- different guest molecules
- no changes due to guests

Die Leitfähigkeit der Cetineite

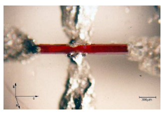


Photoleitfähigkeit:

Substanz	Experiment	Theorie
(K;Se)	2.03 eV	2.2 eV
(Na;Se)	2.12 eV	2.4 eV
(K;S)	2.29 eV	2.5 eV
(Na;S)	2.38 eV	2.6 eV

Anisotropie $\sigma_\perp : \sigma_\parallel$

Experiment: 1 : 30
Theorie: 1 : 10



- **photoconductivity** of (Na;Se)
- good agreement of onset
- theory underestimates anisotropy (effect of guests?)