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Topotactic Formation and Exchange Reactions of Hydrated Layered Tin Sulfides $A_x(H_2O)_ySnS_2$

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Reduction of tin disulfide SnS_2 leads in a reversible topotactic reaction to the formation of layered hydrated phases $A_x^+(H_2O)_y[SnS_2]^{x-}$. The latter exhibit polyelectrolyte character, i. e. ion exchange and solvent exchange reactions as a consequence of the high mobility of the interlayer species. Structure and properties of the tin sulfide hydrates are closely related to those of transition metal dichalcogenide hydrates.

(Keywords: Intercalation compounds; Ion exchange; Layered chalcogenides; Tin sulfides)

Topotaktische Bildung und Austauschreaktionen von hydratisierten Zinnsulfiden $A_x(H_2O)_ySnS_2$ mit Schichtstruktur

Die Reduktion von Zinndisulfid führt in einer reversiblen topotaktischen Reaktion zur Ausbildung von hydratisierten Phasen $A_x^+(H_2O)_y[SnS_2]^{x-}$ mit Schichtengitterstruktur. Diese weisen Polyelektrolytcharakter auf, d. h. sie zeigen Ionenaustausch- und Lösungsmittelaustausch-Reaktionen als eine Folge der großen Beweglichkeit der Moleküle zwischen den Schichten. Struktur und Eigenschaften der Zinnsulfid-Hydrate stehen denen der Übergangsmetalldichalkogenid-Hydrate sehr nahe.

Introduction

Reduction of the electronically conducting layered transition metal dichalcogenides MX_2 (M = transition metal, X = chalcogen) in aqueous electrolytes is known to result in the topotactic formation of hydrated phases by the uptake of cations A^+ into the interlayer space according to eq. (1)[1].

$$MX_2 + x\,A^+ + x\,e^- + y\,H_2O \longrightarrow A_x^+(H_2O)_y[MX_2]^{x-} \qquad (1)$$

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In terms of chemical reactivity these compounds are characterized by their polyelectrolyte nature i.e. cation and solvate characterized by their polyelectrolyte nature i.e. cation and solvate exchange capacity[2]. Among the main group elements only the dichalcogenides of tin SnX_2 are known to crystallize in an undistorted CdI_2 type layer lattice. We were interested in whether these phases which contain a metal with fully occupied *d*-orbitals are able to show similar redox reactions as the corresponding transition metal compounds. In this communication we present our results of an investigation on the redox properties of tin disulfide SnS_2.

Methods

Polycrystalline samples and single crystals of tin disulfide were prepared from the elements in evacuated quartz ampoules by vapor phase transport with iodine in a temperature gradient of 650-550 °C[3]. Reduction and cation exchange were performed in suspensions of polycrystalline SnS_2 in aqueous electrolyte solution. Standard wet methods and flame spectrophotometry served for analysis of Sn, S, alkali and alkaline earth ions. If not otherwise stated all reactions were carried out at ambient temperature under an atmosphere of inert gas. X-ray powder data (CuK_α) were obtained usually from suspensions of the hydrated phases under $1M$ equilibrium solutions. The preparation of alkali metal intercalation compounds of SnS_2 has been described by *Rouxel*[4].

Results and Discussion

On reduction of SnS_2 in aqueous suspensions of K^+, Rb^+ or Cs^+ dithionite the yellow crystals of the starting material slowly change to a dark black color. Observation of this process under the miscroscope shows that the reduction starts at the prism edges of the crystals. No reaction was found in the presence of Li^+ as the cation, whereas slow reaction takes place with Na^+ dithionite as the reducing agent. Single crystals retain their morphology in the course of the reduction. Analytical results show that the products contain alkali, H_2O, tin and sulfur; they can be indexed on a hexagonal base. In suspensions of aqueous electrolyte solutions rapid ion exchange reactions were observed. Lattice parameters of alkali and alkaline earth phases received by ion exchange from the K^+ compound are given in Table 1. It is seen that the *a*-axes values correspond closely to that for SnS_2 ($a = 3.64$ Å). The *c*-axes parameter which amounts to 5.90 Å in SnS_2 is, however, significantly increased in the hydrated alkali and alkaline earth derivatives by uptake of water and cations into the interlayer space. The distance *d* between neighbouring SnS_2 layers corresponds to $c/3$ as it does for the alkali intercalation compounds of tin disulfide reported

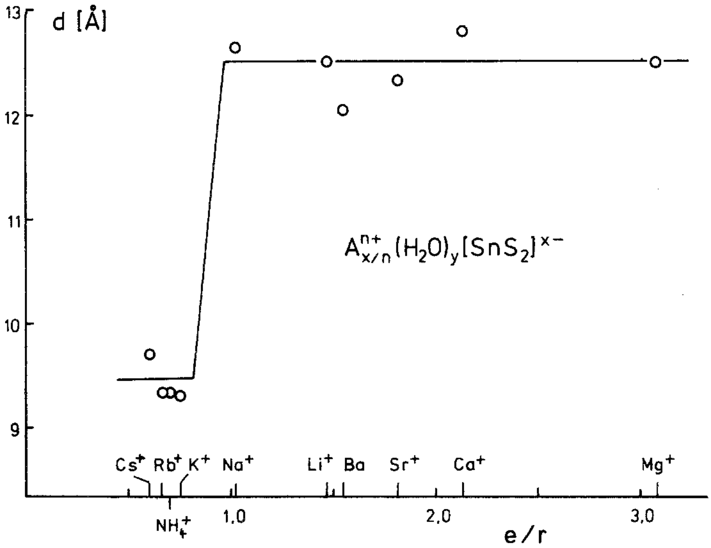

Fig. 1. Correlation between the interlayer distance *d* and the charge/radius ratio for a series of exchangeable cations

Table 1. *Hexagonal lattice constants, interlayer spacings d and interlayer space heights* Δd *of hydrated phases* $A^{n+}_{x/n}(H_2O)_y[SnS_2]^{x-}$

A^{n+}	a (Å)	c (Å)	d	Δd
Li^+	3.71	37.50	12.50	6.60
Na^+	3.72	37.97	12.64	6.74
K^+	3.69	27.90	9.30	3.40
NH_4^+	3.68	27.99	9.33	3.43
Rb^+	3.71	27.96	9.32	3.42
Cs^+	3.74	29.16	9.72	3.82
Mg^{2+}	3.70	37.46	12.48	6.58
Ca^{2+}	3.70	38.42	12.80	6.90
Sr^{2+}	3.69	36.93	12.31	6.41
Ba^{2+}	3.69	36.05	12.02	6.12
Ni^{2+}	3.63	51.77	17.25	11.35

by *Rouxel*[4]. If an interlayer height $\Delta d = d - d_0$ is defined with d_0 being the *Van der Waals* thickness of the SnS_2 layer (5.90 Å), one can see that Δd is strongly dependent on the exchangeable cation A^+ (Table 1). This behaviour is similar to that of the hydrated transition metal chalcogenides and was interpreted by us in terms of the formation of monolayer (Δd ca. 3 Å) resp. bilayer hydrates (Δd ca. 6 Å)[2]. Although the d values are generally somewhat larger in the SnS_2 case, it is obvious from the correlation between the charge/radius ratio of the exchangeable cations A and the interlayer distance d (Fig. 1) that the hydration energies of the interlayer cations essentially determine the hydrate stage. The values found for the negative layer charge density in the alkali series $A_x^+(H_2O)_y[SnS_2]^{x-}$ on the basis of alkali content range between $x = 0.1$ to $x = 0.3$; the actual value may be higher, since protolysis occurs on washing of the samples with water to remove excess electrolyte. Interlayer distance and water content were found to depend in a reversible reaction on ambient water vapor pressure and on electrolyte concentration. The d-value of e. g. $Li_x^+(H_2O)_y[SnS_2]^{x-}$ which amounts to 12.50 Å in $1N$-LiCl solution decreases to 8.93 Å in saturated aqueous LiCl which corresponds to the monolayer hydrate stage. Similarly, on reducing p_{H_2O} above centrifuged samples, monolayer hydrates can be obtained from Li^+, Na^+ and alkaline earth forms. On storing e. g. the Na^+ form in a dry nitrogen atmosphere, the interlayer spacing decreases from 12.64 Å to 8.97 Å. Further removal of the water is possible at 30–50 °C and 10^{-3} Torr: the d-value of e. g. the K^+ form decreases under these conditions from 9.29 Å (monolayer hydrate) to 8.63 Å; this value is closely similar to that reported for the nonhydrated ternary phase $KSnS_2$ (8.53 Å)[4], the small difference in d being due to the higher alkali content of the latter compound. Since Li^+ and Na^+ forms may be obtained easily by ion exchange, we attribute the lack of reactivity with Li dithionite and the slow reaction with Na dithionite to kinetic effects originating from the large effective radius of these strongly hydrated ions.

Ion exchange reactions were found to proceed with a large number of inorganic and organic cations. Small transition metal cations such as Ni^{2+} lead to interlayer spacings which can be interpreted in terms of multilayer hydrates (Table 1), whereas the d-values of organic cations are largely determined by the cation geometry. This is particularly apparent in the case of strongly anisometric cations: for n-alkylammonium ions which form cation bilayers as described earlier for hydrated Mo sulfides[5] interlayer spacings are found between 10.2 Å ($CH_3NH_3^+$) and 36.4 Å ($C_{18}H_{37}NH_3^+$) depending on the length of the alkyl chain. As to be expected from a polyelectrolyte type system water molecules also may be exchanged for inorganic and organic molecules of adequate polarity. The sodium form $Na_x^+(H_2O)_y[SnS_2]^{x-}$ rapidly exchanges H_2O e. g. for formamide (*FA*), N-methylformamide (*NMF*) and dimethylsulfoxide (*DMSO*); the interlayer distance in the resulting solvates is increasing considerably to higher values as a consequence of the increased solvent dimensions: $d(FA) = 15.80$ Å, $d(NMF) = 17.35$ Å and $d(DMSO) = = 17.77$ Å.

The compounds described are susceptible to oxidation; all reactions were therefore carried out in an atmosphere of inert gas. The oxidation process is equivalent to the reversion of eq. (1) and can be performed e. g. by treatment of suspensions of the hydrated phases with dioxygen. Kinetics are dependent on the *pH* value: the reaction velocity increases with decreasing *pH*. The color of the solid changes during oxidation from black to yellow; the final product SnS_2 was identified by its powder pattern.

On extended reduction with dithionite, the diffraction lines of a new phase was observed with after a few days is left as the only solid product. Analysis and X-ray investigation of this black phase showed that pure tin monosulfide SnS was formed in an irreversible process. Attemps to obtain the hydrated phases by cathodic reduction lead to inhomogeneous products with the presence of unreacted starting material.

Rouxel et al. observed in the course of an investigation on the alkali metal intercalation compounds $ASnS_2$ that on reaction of these phases with water hydrogen is evolved and SnS_2 is obtained along with alkali hydroxide[4]. The authors isolated a hydrated compound on treatment of $KSnS_2$ with water vapor of 10 Torr for which they give a composition $K(OH)(H_2O)SnS_2$ with the hexagonal axes $a = 3.65$ Å and $c = 25.8$ Å. We found that $NaSnS_2$, prepared according to *Rouxel*, reacts in liquid NH_3 at —30 °C with H_2O to give a hydrate that after washing with water shows a powder pattern which is identical with that of $Na_x^+(H_2O)_y[SnS_2]^{x-}$ described above. Similar chemical reactivity was demonstrated by cation exchange reactions leading to alkali and alkaline earth derivatives with hexagonal parameters identical to those given in Table 1.

Conclusions

The results presented reveal that hydrated sulfides of the main group element tin $A_x^+(H_2O)_y[SnS_2]^{x-}$ show basically similar topotactic reactions with respect to solvation, ion exchange and redox behaviour as the hydrated layered chalcogenides of transition metals. Whereas the latter elements are known to be stable in several oxidation states differing by one unit, there remains the question of the oxidation state of Sn in the negatively charged $[SnS_2]^{x-}$ layers. Known oxidation states of tin are +2 and +4; the black color and the redox behaviour suggest that the electronic state of the hydrates may be described in terms of a Sn^{II}/Sn^{IV} mixed valence model. The instability of these phases is demonstrated by the observation that they easily decompose to give the binary sulfide SnS with divalent tin. *Mössbauer* investigations which are projected may help to establish the valence of Sn in these compounds.

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