Topotactic Electron/Ion Transfer Reactions of Niobium Chalcogenides NbX₄ with Tunnel Structure

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Z. Naturforsch. 34b, 697–699 (1979); received February 19, 1979

Topotactic Reactions, Intercalation Compounds, Niobium Chalcogenides, Ionic Conductivity, Superconductivity

Cathodic reduction of NbS₄ and NbSe₄ electrodes in electrolytes containing cations of appropriate size results in the formation of ternary phases Aₓ⁺[NbX₄]⁻橡胶。The cations A⁺橡胶 are taken up into empty channels of the rigid lattice framework and exhibit high ionic mobility at room temperature.

Within the research area of solid state ionics there has been increasing interest during the last years in redox reactions at ambient temperature of electronically conducting phases. These processes are characterized by the reversible synchronous uptake of electrons and of ions (from adjoining electrolytes) into the host structure under conservation of the host lattice matrix (eq. (1)) [1, 2]. Phases showing this type of reactivity are

\[ \frac{x}{n} A^{n+} + xe^- + M \rightarrow A_{\text{eq}}^{n+} [M]e^- \] (1)

(A⁺橡胶 = electrolyte cation; M = host lattice matrix)

of potential interest as novel electrode materials for high energy density batteries [3]. Whereas considerable work has been devoted to the study of compounds with layer and chain structures there are few reports only on solids with three-dimensional framework structure. In a recent investigation we were able to demonstrate that Mo₆X₈ cluster chalcogenides (X = S, Se), which exhibit a three-dimensional interconnected “channel” system of empty lattice sites, may undergo reversible redox reactions [4]. With respect to the well-known susceptibility of one-dimensional systems to point defects and extended defects, we were interested in whether structures with isolated empty channels would still be able to show the type of reaction under discussion.

We selected as model lattice the binary niobium sulfide NbS₄ reported first by Jellinek [5]. NbS₄ (hexagonal, a = 9.5806 Å, c = 3.3747 Å) can be described as being built up by NbS₆ octahedra joined together by common faces and edges to form a three-dimensional framework characterized by wide empty channels which run through the lattice in direction of the c-axis (Fig. 1). The latter should be large enough to accommodate additional atoms.

Preparation was performed from the elements by vapour phase transport with iodine (900 – 1000 °C) leading to needle shaped single crystals up to 10 mm in length. An estimation of the channel diameter from structural data suggested that cations up to the radius of K⁺ (1.33 Å) should be able to enter the lattice. Cathodic reduction of pressed NbS₄ working electrodes under galvanostatic conditions (N₂ atmosphere, 25 °C) in 1 M neutral aqueous solutions of Li⁺, Na⁺, K⁺ and Ca²⁺ showed potential steps corresponding to an electron transfer of 0.2 e⁻/NbS₄. Analytical data of the products demonstrate that NbS₄ is reduced to ternary phases Li₁₋₈NbS₄, Na₁₋₈NbS₄, K₁₋₈NbS₄ and Ca₁₋₈NbS₄. The compounds slowly decompose in air; no uptake of solvent molecules as observed for layered ternary systems in aqueous electrolytes [6] was found. As a consequence of the rigid three-dimensional framework structure lattice constants obtained from powder Guinier diagrams differed for both hexagonal axes only by ± 0.05 Å as compared to the parent lattice. The reaction is fully reversible, anodic oxidation again leading to the formation of NbS₄ (eq. (2)).

* Reprint requests to Prof. Dr. R. Schöllhorn. 0340–5087/79/0500–0697/$ 01.00/0
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\frac{x}{n} A^{x+} + xe^- + Nb_3S_4 \rightleftharpoons A_{3x}^{x+} [Nb_2X_4]^{x-}
\]

The excellent reversibility was demonstrated also by cyclovoltammetric studies which indicate a high ionic mobility inside the lattice channels; peak potentials decreased to more negative values with decreasing ionic radius from K\(^+\) to Li\(^+\) (i.e. with increasing hydration energies of the cations), whereas peak currents decrease with increasing cation radius.

The values calculated for a close packing of e.g. K\(^+\) inside the channels are, however, considerably higher than those observed experimentally. Although electrostatic and electronic aspects could be invoked to account for this observation, an interpretation in terms of a critical susceptibility of the intercalation process to lattice defects has also to be considered. Under these terms a partial accessibility of the total solid volume would result which is indicated schematically in Fig. 2. This is supported by the fact that the stoichiometric index \(x\) for \(A_{2}NbS_4\) is depending on particle size: in the range of average crystallite size (needle cross section) from ca. 1.56 \(\cdot\) 10\(^{-2}\) mm\(^2\) to ca. 1.6 \(\cdot\) 10\(^{-4}\) mm\(^2\) the variation of \(x\) for Na\(^+\) as the cation corresponds to 0.15-0.25.

If one assumes that filling up the empty lattice channels with cations under thermal equilibrium conditions should lead to a stabilized structure without large voids and consequently less disorder, one should expect an increase in accessible channel volume i.e. an increase in the redox range (eq. (2)). Since earlier investigations on the reduction of transition metal chalcogenides in alkali halide melts with alkali metals had proved to be a useful method for the preparation of ternary phases [7], we studied the reaction of NbS\(_2\) and NbS\(_4\) with Na and K in the corresponding chlorides at 800-1000 °C in alumina vessels under argon. The ternary phases thus obtained were Na\(_{0.18}\)NbS\(_2\)S\(_4\) and K\(_{0.65}\)NbS\(_4\) with the hexagonal lattice parameters \(a = 9.564\) Å, \(c = 3.371\) Å and \(a = 9.550\) Å, \(c = 3.372\) Å; they are isomorphous with NbS\(_4\). The relatively low alkali content must be due to partial oxidation during removal of the halide matrix from the product by washing with water. Cathodic reduction of the ternary phases in aqueous Na\(^+\) and K\(^+\) electrolytes led to Na\(_{0.6}\)NbS\(_4\) and K\(_{0.65}\)NbS\(_4\), respectively. We thus observe a significant increase in the degree of filling of the channels which we attribute to a reduced defect concentration in the thermally prepared ternary phases.

The results obtained with NbS\(_4\) demonstrate that chalcogenide structures with isolated channel systems are basically able to undergo reversible topotactic redox reactions. A similar reactivity and high ionic mobility was found for the selenide NbS\(_3\)Se\(_4\). Since NbS\(_4\) and NbS\(_3\)Se\(_4\) undergo a phase transition to the superconducting state at low temperatures [8, 9] – which is likely to be related to the presence of one-dimensional metal clusters in the lattice framework – it will be of interest to find out, if for the NbS\(_4\) system a strong influence of intercalated metal ions on the superconducting properties will be observed comparable to that found in the case of the Chevrel phases M\(_2\)Mo\(_6\)X\(_8\) (X = S, Se) [10]. A systematic study on this subject is presently under way; preliminary measurements show a transition temperature \(T_c = 7.3\) K for K\(_{0.2}\)NbS\(_4\) i.e. an increase in \(T_c\) as compared to the corresponding binary phase.

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