



Li intercalation and anion/cation substitution of transition metal chalcogenides: Effects on crystal structure, microstructure, magnetic properties and Li⁺ ion mobility

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We investigated experimentally the effect of Li intercalation on the structural, microstructural and magnetic properties as well as on the Li ion diffusivity of the complex chalcogenides Cr_{5-y}Ti_ySe₈. In addition, the effect of anion substitution in TiS_{2-z}Se_z on the Li diffusion parameters was studied by ⁷Li nuclear magnetic resonance (NMR) spin-lattice relaxation measurements.

For Cr_{5-y}Ti_ySe₈ the Li⁺ insertion is accompanied by an irreversible phase transition from monoclinic to trigonal symmetry which is electronically driven. The maximal Li content in the host material depends on the Ti content and decreases with increasing y in Cr_{5-y}Ti_ySe₈. The intercalated materials can be deintercalated and the minimal Li content in the residual compound increases with Ti abundance. The intercalation process is accompanied by drastic changes of the microstructure. Electrochemical discharge curves depend significantly on the Ti. According to the results of XANES investigations performed on Cr₄TiSe₈, Ti is first reduced during Li uptake and Cr atoms accept electrons at later stages of the intercalation reaction. *In-situ* energy dispersive X-ray diffraction experiments show that the Li intercalation at room temperature proceeds via two different mechanisms while intercalation at 60 °C is faster and is dominated by one mechanism. ⁷Li MAS NMR measurements revealed a variety of transition metal environments around the Li sites corresponding to the Cr/Ti disorder. The NMR studies also indicate fast Li dynamics. The magnetism of the educts is dominated by strong antiferromagnetic exchange interactions in the high temperature region and by spin-glass behavior in the low temperature range. Intercalation of Li weakens the antiferromagnetic exchange and for fully intercalated materials ferromagnetic exchange is observed. The interpretation of the experimental results is supported by accompanying band structure calculations.

In layer-structured Li_xTiS_{2-z}Se_z (x ≈ 0.7) the Li diffusivity was investigated by various NMR techniques and compared with results obtained for the pure end members Li_xTiS₂ and Li_xTiSe₂. In particular, anion substitution clearly influences the slopes of the low-*T* flanks of the diffusion induced NMR relaxation-rate peaks. The corresponding activation barriers characterizing local hopping processes are reduced in the mixed samples with 0 < z < 2 and can be explained by a domain model. DFT calculations yield very small hopping barriers along S-rich and Se-rich domain boundaries while the barriers for Li migration inside the domains are rather high. It is therefore assumed that Li migrates along the domain boundaries.

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1. Introduction to intercalation chemistry

Intercalation and deintercalation are the basic chemical reactions occurring in Li batteries. Most of the publications concerning the synthesis and characterization of new battery materials deal with oxides, phosphates, carbon-based materials, silicon, silicon alloys and nanosized particles [1–5]. A new approach for the preparation of Li battery materials uses conversion reactions, *i.e.* $\text{M}^{n+}\text{X}_y + z\text{Li} \rightarrow \text{M}^0 + y\text{Li}_n\text{X}$ (M = metal, X = non-metal) for charging and the reverse reaction for discharging [6,7].

However, intercalation/deintercalation reactions are also a powerful synthetic approach which was introduced a long time ago, and the state of the art is summarized in several monographs [8]. The great advantage of intercalation and deintercalation processes is that they proceed under ambient conditions enhancing the chance for the synthesis of metastable compounds which cannot be prepared applying classical synthesis methods. Using this method unusual oxidation states can be stabilized such as Cr^{4+} in CrSe_2 [9], or structures can be obtained such as the Nb_3Se_4 structure of Ti_3Se_4 [10] as well as V_3S_4 [11]. Besides the synthesis of new and metastable inorganic materials, intercalation reactions are a powerful synthetic approach for the generation of inorganic–organic hybrid materials [12], pillared materials [13] or new electrode materials [14]. Performing the intercalation reaction with a conducting host material the intercalation process is accompanied by an electron transfer from the guest to the host material altering the physical properties of such host–guest complexes [15]. Because

the intercalation proceeds under ambient conditions under kinetic control, the amount of intercalated guest species can be controlled and therefore the physical properties can be tuned in a directed way. In the field of chalcogenides prominent examples are Chevrel phases [16] or compounds with the Nb_3Se_4 -type structure containing nanosized one-dimensional channels. Intercalation of these compounds is accompanied by significant changes of the electric conductivity and superconducting properties [17]. In the past we demonstrated that intercalation/deintercalation is a suitable synthetic approach for the stabilization of unusual oxidation states like in TiCr_5Se_8 where the removal of Ti^+ induces the oxidation of Cr^{3+} to Cr^{4+} [18] or to the formation of valence band holes [19]. Intercalation/deintercalation is not restricted to simple host structures, also complex thiophosphate materials were already investigated [20].

Besides the numerous oxygen-based materials many different host materials such as TiS_2 (see below) were intensively studied as electrode materials for battery applications [[21]; see also several chapters of the monographs]. More recently, several groups started to investigate the reaction of Li with more complex materials like CuTi_2S_4 , CuCr_2S_4 [22], $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ [23], $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$, $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ [24] or $\text{Sr}_2\text{MnO}_2\text{Cu}_{2m-0.5}\text{S}_{m+1}$ ($m = 1, 2, 3$) [25], to name just a few. In some systems the intercalation of guest ions is accompanied by a combined displacement/intercalation (CDI) reaction as observed for, *e.g.*, $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ [26]. During the intercalation process one of the metals is reduced and then extruded from the host material. Using the thiospinels CuTi_2S_4 or CuCr_2S_4 the insertion of

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