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Facile synthesis, structure and physical properties of 3*R*-A_xNbS_2 (A = Li, Na)

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ABSTRACT

Here we report the facile synthesis of alkali metal intercalation compounds A_xNbS_2 (A = Li, Na) through the reaction of bulk 3*R* phase of NbS_2 with organometallic compounds in solution. Especially, the Na insertion compound of various compositions was obtained as a new polytype of A_xNbS_2 compared with the 2*H* phase reported previously. Upon intercalation the structure of the host was preserved, which was confirmed by XRD and HRTEM analysis. The interlayer distances for $Li_{0.44}NbS_2$ and $Na_{0.87}NbS_2$ were expanded by 0.187 Å and 0.938 Å as a result of Li and Na intercalation, respectively. The electrical transport properties were studied in the temperature range 4–298 K, exhibiting metallic conductivity and slight variation in the resistivity value in general. Interestingly, a minimum resistivity which was ascribed to the localized electrons in the crystal lattice emerged for all the investigated samples.

1. Introduction

Transition metal dichalcogenides (TMDs) with lamellar structures have received considerable attention because of their versatile chemistry displaying during the intercalation process which involves crystallographic transformation and modification of physical properties by introducing guest atoms or molecules into the host lattice [1–4]. As a typical member of layered TMDs, niobium disulfide (NbS_2) has three polytypes: 1*T*, 2*H* and 3*R*, according to the different stacking sequences and numbers of S—Nb—S units in the unit cell [5–7]. In fact, the latter two polymorphs are confirmed to be the only stable ones in contrast to the 1*T*. It is well-established that both crystal lattice and electrical conductivity can be tuned via alkali metal intercalation with respect to the electron transfer between the alkali metal and the transition metals for various materials [8–10]. Up to now, several methods have been employed to synthesize alkali metal intercalation compounds represented by the formula A_xNbS_2 (A = alkali metal) based on the solid-state processes, such as heating the mixtures of elements or compounds [11,12], metathesis using ternary oxide precursor [13,14], and crystallization from the binary alkali-metal sulphide melt [15]. The compounds obtained through the above one-step processes are made of two NbS_2 slabs per unit cell with alkali metal ions intercalated between them, namely 2*H* phase. Due to the layered framework as intrinsic ion channel and Nb(IV)/Nb(III) redox couple, both the 2*H* and 3*R*—NbS_2 were chosen as electrode materials for Li-ion battery to characterize their electrochemical performance [16–18]. In addition, Na-insertion/extraction reaction was carried out for the system 2*H*-Na_xNbS_2 ($0 \leq x \leq 1$) as Na-ion battery [19]. However, no experimental results offer direct evidence on the fabrication of other alkali metal (Na, K etc.) intercalation compounds of bulk 3*R*—$Nb_{1+x}S_2$ and their related physical properties with an assumption that the introduction of guest species was restricted by the existence of rich niobium atoms in the interlayer gallery. Therefore we focus attention on the design and synthesis of novel alkali metal intercalation compounds of 3*R*—$Nb_{1+x}S_2$ to explore the hidden traits of this non-stoichiometric host.

In comparison with solid-state reaction, solution-phase process conquers the limits of difficulty in controlling the composition and preparing homogenous samples. For instance, n-butyllithium diluted in hexane solution has been used as a typical lithium reactant to prepare abundant Li insertion compounds of layered TMDs [20]. Recently, high yield exfoliation of TMDs has been

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achieved using sodium naphthalenide, which is formed as one dark green radical anion solution by dissolving the sodium with hydrocarbon molecule (naphthalene) in polar organic solvent [21]. The distinct reducing ability and wide application scope make these alkali metal-aromatic hydrocarbon adducts stand out and provide us a favourable strategy to introduce various alkali metals into the layered framework by disrupting the weak van der Waals force. Plentiful results have been completed engaging these peculiar adducts in the ternary metal nitride halides MNX (M = Zr, Hf; X = Cl, Br, I) system [9,10,22]. Herein, we started with the preparation of bulk 3*R*–$Nb_{1+x}S_2$ and then synthesized the alkali metal intercalated compounds 3*R*-A_xNbS_2 (A = Li, Na) of various compositions using alkali metal naphthalide solution. The host structure remained upon Li and Na intercalation, meanwhile, the interplanar spacing was substantially expanded. The resistivity and magnetic susceptibility measurements were carried out for the pristine and intercalated materials. To the best of our knowledge, the present work offers the facile synthesis of 3*R*-Na_xNbS_2 by a room temperature solution-phase process for the first time.

2. Experimental section

2.1. Synthesis of bulk 3R–$Nb_{1+x}S_2$ and its alkali metal intercalation compounds A_xNbS_2 (A = Li, Na)

In a typical synthesis, 0.464 g (5.00 mmol) of niobium powder and 0.320 g (10.00 mmol) of sulfur powder were well ground. The mixture was then sealed in an evacuated quartz tube, 10 cm in length and 0.8 cm in diameter. The tube was heated to 900 °C at a rate of 5° C min^{-1} in a muffle furnace, allowed to react at 900° C for 2 days, and then cooled down to room temperature naturally. Owing to the temperature gradient inside the furnace, the target product with metallic grey luster was obtained at one end of the tube, while unreacted yellow sulfur was condensed in opposite end of the tube which can be separated easily.

For the intercalation process, pristine $Nb_{1+x}S_2$ powder was dispersed into solution of alkali metal naphthalenide with concentrations ranging from 0.05 to 1 M, prepared by dissolving equal molar amounts of alkali metal and naphthalene into anhydrous tetahydrofuran (THF) in an argon atmosphere. The reaction flask was sealed tightly and allowed to react completely at room temperature. Then the suspension was centrifuged and washed with fresh THF to remove the soluble organic by-product. Finally the as prepared products were dried under vacuum in inert gas atmosphere. We investigated the effects of experimental parameters on the intercalation behaviour of this self-intercalated host by modifying the molar ratio of the alkali metal to the host in the range of 0.5–15, regulating reaction time for 1–7 days.

2.2. Etching the fresh alkali metal intercalated compounds with ethanol

The fresh alkali metal intercalated compounds showed apparent hygroscopic properties in atmospheric environment, partly due to the absorbed alkali metal ions on the surface of samples which couldn't be washed completely by THF. As ethanol has been demonstrated to play an interesting role in controlling the amount of alkali metal ions doped in the layers divulging in graphite [23], we etched the fresh samples with absolute ethanol. The products were dried under vacuum at 60° C for further characterization.

2.3. Materials characterization

The samples were characterized by powder X-ray diffraction (XRD) on a Philips X'pert X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F scanning electron microscope. High-resolution transmission electron microscope (HRTEM) images, selected area electron diffraction (SAED) patterns were taken on a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. The non-stoichiometric feature of the host was confirmed by elemental analysis on the Vario EL III. Elemental ratios of alkali metal to niobium were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using Atomscan Advantage. Magnetic measurements were recorded on SQUID-VSM (Quantum Design), operating at an applied magnetic field of 0.01 T and in the temperature range from 4 K to 300 K. The standard four-probe method was used to test the resistivity of the samples in the temperature range between 4 K and 298 K using VSM (Cryogenic Limited). Specifically, by employing a custom-made mould, four copper wires (0.2 mm in diameter) were embedded in the sample pellets at equal distance. Tin solder was then utilized to establish the electrical connection between sample and specimen holder.

3. Results and discussion

3.1. X-ray diffraction and TEM analysis

Fig. 1 shows the X-ray diffraction patterns of typical samples. The cell dimensions were determined by indexing the reflections based on *R*3*m* space group. All the reflections exhibited in Fig. 1a could be indexed with lattice parameters $a = b = 3.328(2)$ Å, $c = 17.906(6)$ Å, in agreement with those of $Nb_{1.06}S_2$ (PDF #41–1318). Furthermore, the elemental analysis as shown in Table S1 was performed to evaluate the composition of the host, confirming the Nb-rich nature of the obtained samples. For simplicity, we use formula NbS_2 instead of $Nb_{1+x}S_2$ with different x values between 1.08 and 1.11 determined within the accuracy limits of our instrument in the following description. Upon Li and Na intercalation, all the peaks belonging to *00l* reflections shifted to lower angles in a regular manner as shown in Fig. 1b–c, manifesting the expansion of cell dimension along the *c* axis. The patterns for $Li_{0.44}NbS_2$ and $Na_{0.87}NbS_2$ can be indexed with lattice parameters $a = 3.330(6)$ Å, $c = 18.468(8)$ Å;

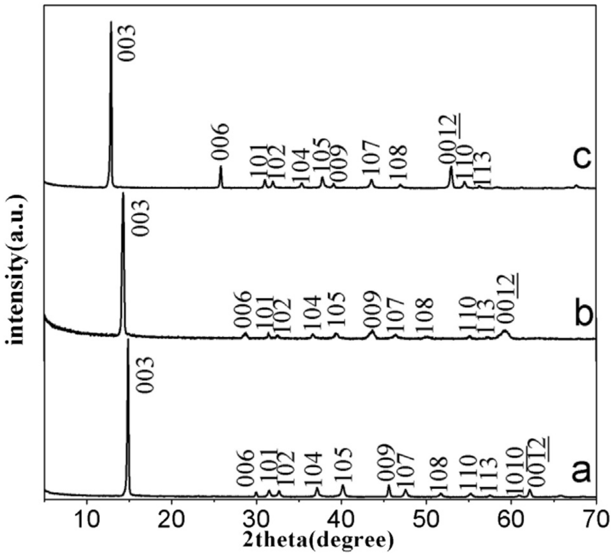

Fig. 1. Typical XRD patterns for: (a) 3*R*–$Nb_{1+x}S_2$; (b) the lithium insertion sample $Li_{0.44}NbS_2$; (c) the sodium insertion sample $Na_{0.87}NbS_2$.