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Preparation and characterization of colloidal dispersions of layered niobium chalcogenides

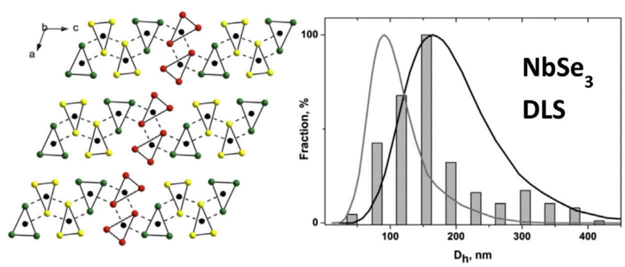
Sofya B. Artemkina [a,b,*], Tatyana Yu Podlipskaya [a], Alexander I. Bulavchenko [a], Alexander I. Komonov [c], Yuri V. Mironov [a,b], Vladimir E. Fedorov [a,b]

[a] Nikolaev Institute of Inorganic Chemistry SB RAS, 3, Akad. Lavrentiev Ave., 630090 Novosibirsk, Russian Federation
[b] Novosibirsk State University, 2, Pirogova Str., 630090 Novosibirsk, Russian Federation
[c] Rzhanov Institute of Semiconductors SB RAS, 2, Akad. Rzhanov Str., 630090 Novosibirsk, Russian Federation

HIGHLIGHTS

- Niobium chalcogenides NbQ_2 and NbQ_3 can be regarded as layered materials.
- NbQ_2 and NbQ_3 were exfoliated by ultrasonication forming colloidal dispersions.
- Particles size distributions in the dispersions were analyzed by DLS and AFM methods.
- Films prepared from the dispersions demonstrate the initial NbQ_2 and NbQ_3 structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Stable colloidal dispersions of niobium chalcogenides NbQ_2 and NbQ_3 (Q = S, Se) in organic solvents – CH_3CN, dmf, $^{i}PrOH$, EtOH, EtOH/H_2O (vol. 1/1), *n*-BuOH were prepared by ultrasonication. According to DLS and AFM data the particle size distributions in the dispersions are rather wide: particle sizes vary from 70 to 400 nm, and the mean sizes are in range of 150–200 nm. DLS polymodal and monomodal analyses were carried out for the colloidal dispersions of NbQ_2 and NbQ_3 (Q = S, Se) in acetonitrile. The particles diffusive Brownian motion in the acetonitrile colloidal dispersions is best described by diffusion of disk-shaped particles with monomodal distributions for NbQ_3 and bimodal distributions for NbQ_2. A series of thin films prepared from the colloidal dispersions show that the particles retain their original crystal structures, at the same time strong texturing of the films appears.

1. Introduction

A considerable world-wide interest in nanomaterials currently exists, and of particular interest are the methods of preparation of nanomaterials. Transformation of bulk materials into colloidal dispersions and subsequent formation of films or compact samples from the dispersions is one of the promising ways of "top-down" methods in the preparation of nanomaterials. This method becomes particularly effective in the case of compounds with layered structures, for example, exfoliated graphene [1] and a series of transition

Abbreviations: TMDC, transition metal dichalcogenides; TMTC, transition metal trichalcogenides; AFM, atom-force microscopy; DLS, dynamic light scattering.

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry SB RAS, 3, Akad. Lavrentiev Ave., 630090 Novosibirsk, Russian Federation.
Tel.: +7 383 330 92 53; fax: +7 383 330 94 89.

E-mail addresses: artem@niic.nsc.ru (S.B. Artemkina), tatyanap@niic.nsc.ru (T.Y. Podlipskaya), bulavch@niic.nsc.ru (A.I. Bulavchenko), komonov@isp.nsc.ru (A.I. Komonov), yuri@niic.nsc.ru (Y.V. Mironov), fed@niic.nsc.ru (V.E. Fedorov).

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metal dichalcogenides MQ_2 (M = Ti, Zr, Hf; V, Nb, Ta, Mo, W; Q = S, Se) (TMDC) [2].

In our work, we have consider the preparation of colloidal di- and trichalcogenides of niobium – NbQ_2 and NbQ_3 (Q = S, Se). Niobium dichalcogenides (NbS_2 and $NbSe_2$) belong to the well-known family of layered TMDC. In the crystal structures of these dichalcogenides polymeric layers of covalently bonded metal and chalcogen atoms "Q–Nb–Q" interact with the neighboring layers only via van der Waals Q. . .Q forces (Fig. 1). The weak van der Waals interactions are responsible for the very well-known property of TMDC – easy sliding of the layers relatively to each other; owing to this, such materials find themselves as dry lubricants. Layered dichalcogenides provide a favorable matrix for intercalation reactions. This property allows exfoliating the compact materials to oligolayered structures down to single-layered ones.

According to structural and spectroscopic data, niobium trichalcogenides NbQ_3 (Q = S, Se) may be described by the ionic formulation $Nb^{4+}(Q_2)^{2-}Q^{2-}$, which contains two types of non-equivalent chalcogen atoms – chalcogenide Q^{2-} ions and dichalcogenide groups $(Q_2)^{2-}$. Although a prism $\{NbQ_{6/2}\}$ is a basic structural fragment for niobium dichalcogenides and trichalcogenides, NbQ_3 are described by more complicated structures (Fig. 2). Nonequivalence of the chalcogen atoms in NbQ_3 results in formation of distorted (wedge-shaped) prisms where the shortened distances Q–Q point at the dichalcogenide groups ${Q_2}^{2-}$. Such prisms $\{NbQ_{6/2}\}$ with metal atoms situated close to the prism centers are connected to each other via common triangle bases to form infinite columns which are oriented along the *b* axis. Additionally, these columns are connected to the neighboring ones forming corrugated layers two prisms thick. Hence the crystallochemical analysis of NbQ_3 structures allows them to be considered as layered materials. Similarly to NbQ_2, in NbQ_3 structures polymeric layers are connected to each other through van der Waals interactions.

Despite the NbS_3 and $NbSe_3$ crystal structures having some common features, each compound possesses its own specific crystallochemical and electronic characteristics. Thus in the structure of monoclinic $NbSe_3$ there are three sorts of wedge-shaped columns which differ from each other by the electronic properties of the Se_2 groups [3], whereas all the columns are equivalent in the triclinic NbS_3 [4]. It is important to note that in the metallic phase of $NbSe_3$ the chains – Nb–Nb–Nb – are equidistant due to partial charge transfer from niobium atoms to the diselenide groups, whereas in NbS_3 the ions Nb^{4+} form binuclear clusters (with d^1–d^1 bonds) that results in the semiconductor property of niobium trisulfide NbS_3.

Layered transition metal chalcogenides have great attention because of their electronic properties: among the compounds one can find semiconductors as well as compounds with metallic properties including superconduction. TMDC are considered as having the potential for preparing materials for microelectronics and optoelectronics, and they also possess the substantial possibility for application as solar cell elements, lithium batteries, in catalysis, nanotribology and other areas [5]. Transition metal trichalcogenides (TMTC) are interesting because they display such intriguing properties as Peierls instability ("metal-dielectric" transition), formation of charge density waves (CDW) as well as other uncommon phenomena stipulated by the dynamics of electron condensate CDW [6–16].

The layered structure of such compounds allows them to be exfoliated which produces material particles with different thickness down to single layers. To date a considerable number of publications dealing with TMDC exfoliation have appeared [2,17]. Mechanical exfoliation and dispersion of the solids in solution are well-known exfoliation methods. The solution methods allow for the procedure to be carried out on a large scale, so they may be regarded as being more versatile ones. However, unlike TMDC, TMTC crystallize as very thin fibers.

There are no publications on exfoliation of TMTC. The idea of considering TMTC as layered materials as proposed here permits one to consider that these exfoliated materials will be of interest along with TMDC materials.

We present in this report the results of exfoliation of niobium chalcogenides (NbS_2, $NbSe_2$, NbS_3, $NbSe_3$) in different solvents as well as a study of their colloidal dispersions obtained by ultrasonication.

2. Materials and methods

2.1. Methods and apparatus

X-ray powder diffraction patterns for solids including film samples were collected with a Philips PW 1830/1710 automated diffractometer (Cu K_α radiation, graphite monochromator, silicon plate as an external standard). Raman spectra were recorded with a Triplemate spectrometer. UV spectra were recorded with an Ultraspec 3300 pro spectrometer in the range of 200–1100 nm. Exfoliation of trichalcogenides in organic solvents was carried out in an Elmasonic S40 ultrasonic bath (ultrasound power 120 W, frequency 37 kHz). An Eppendorf Centrifuge 5430 equipped with containers for 15 and 50 ml vials was used for centrifugation of the sonicated mixtures. Each colloidal dispersion was prepared at least 5 times for checking the reproducibility of the experiments and concentration averaging.

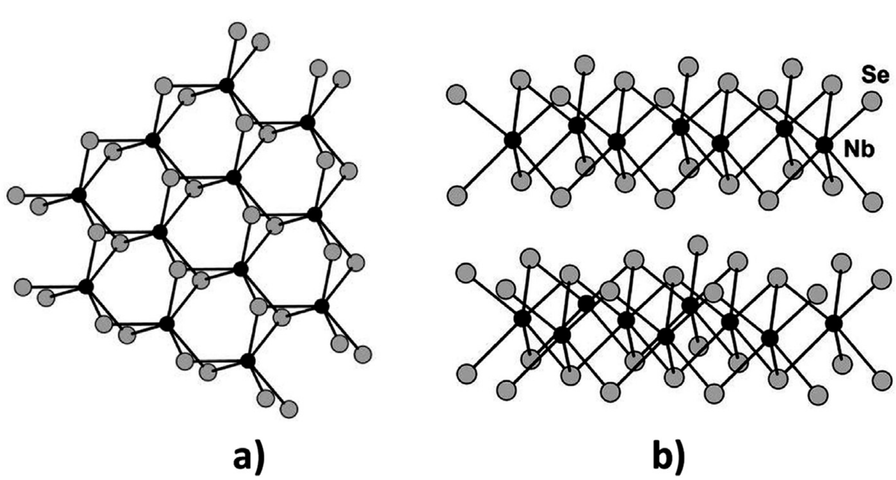

Fig. 1. Structure of the polymeric layer (a) and relative arrangement of the layers (b) in the crystal structure of trigonal $NbSe_2$ (ICSD-18131).