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Top-down synthesis and characterization of exfoliated layered $KLnS_2$ (Ln = La, Ce, Gd, Yb, Lu) nanosheets, their colloidal dispersions and films

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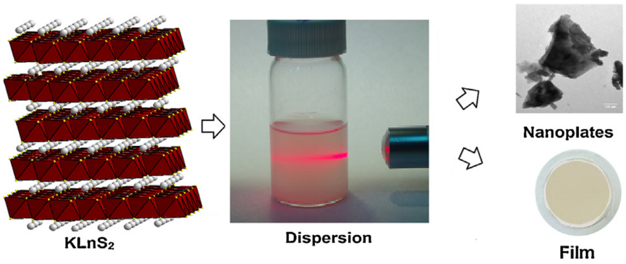
HIGHLIGHTS

- Stable dispersions of $KLnS_2$ can be obtained by ultrasonic treatment.
- In colloids nanoparticles exist as thin nanoplates with high side-to-thickness ratio.
- Films, prepared from dispersions, were high-textured samples of $KLnS_2$.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time the top-down approach was successfully applied to obtaining rare-earth sulfide nanoparticles. In this work we demonstrated that stable dispersions of $KLnS_2$ (Ln = La, Ce, Gd, Yb, Lu) can be prepared by liquid exfoliation by ultrasonic treatment in polar organic solvents. The isopropanol and acetonitrile dispersions demonstrated the highest concentrations and stability among used solvents. The colloids contain thin nanoplates of rhombohedral $KLnS_2$. According to TEM and AFM data, the lateral particles' sizes were 50–600 nm with thickness 3–15 nm. By filtering the nanoparticles can be reassembled as films, demonstrating strong texture along *00l* direction.

1. Introduction

Nanotechnology is one of the most active developing fields of chemistry. The potential of this technology ensures us to manipulate materials at the nanometer scale, resulting in new tools from nanoparticle catalysts [1] to high performance composites [2,3], and thus, nanotechnology opens up new frontiers for innovation in medicine [4], electronics, materials, etc. [5,6]. A considerable number of studies have been focused on the preparation of various classes of inorganic substances, and intense progress had been made in the synthetic control of the size and shape of diverse nanostructures [7–10]. A lot of covering reviews of different aspects of synthesis and applications of the nanomaterials were published up to date [11–14].

Rare-earth based nanoparticles have attracted widespread attention due to unique 4*f*-configuration and associated physical properties. There are numerous examples of luminescent [15,16],

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Abbreviations: TEM, transmission electron microscopy; AFM, atom-force microscopy; DLS, dynamic light scattering; XRD, X-ray diffraction; IPA, isopropyl alcohol; EDX, energy-dispersive X-ray spectroscopy.

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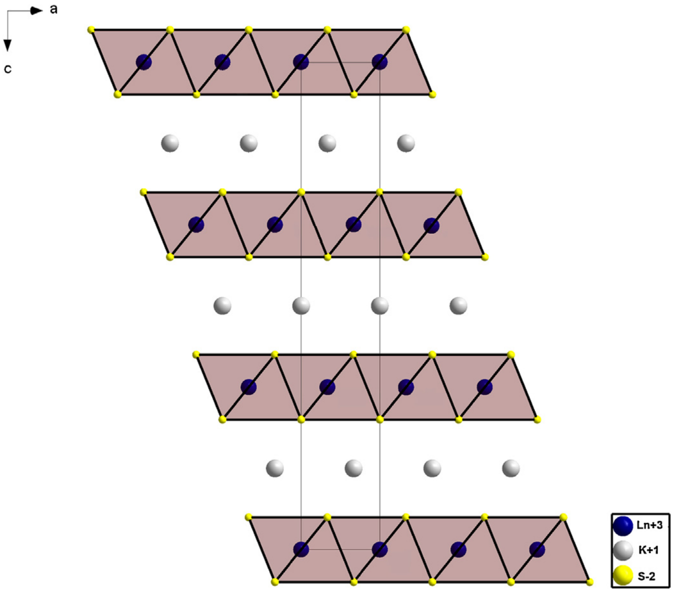

Fig. 1. Crystal structure of $KLnS_2$.

scintillating [17,18], bioimaging [19,20] catalytic [21], magnetic [22,23] lanthanide nanomaterials examples. Among this plethora, there is lack of nanoparticles with Ln-Q bonds, where Q = S, Se, Te. The explanation of this fact can be found at hard soft acid base theory (HSAB) [24]. According to this, hard ion Ln^{3+} make bonds easier with hard ions (O^{2-}, F^-) than with relatively soft Q^{2-}. Due to high oxophilicity of lanthanides, conventional methods applied to other lanthanide nanoparticles (sol-gel, spray-pyrolysis, hydrothermal, etc.) in case of chalcogenides can lead to hydrolysis to oxygen-containing products. Only few works are known about such nanoparticles; there are reports of divalent chalcogenides EuS [22,25,26] and EuSe [27], nanowires Sm_2S_3 [28], ternary nanocubes and nanodiscs $NaLnS_2$ [29], and one article is about Ln^{3+} selendides [30].

One of the effective synthetic approach for manufacturing nanoparticles is liquid exfoliation [31]. This technique can be applied to various layered materials, including those with charged layers like clays [32] and layered double hydroxides [5,33]. Exfoliation by ultrasonic treatment allows obtaining few-layer or single layer materials. It also can be provided at large scale making this method versatile. In this work, we present the top-down synthesis of $KLnS_2$ nanosheets by liquid exfoliation and characterization of their colloidal dispersions in different solvents. Structural similarities with layered double hydroxides and niobates, which have been exfoliated [34,35] allowed to suggest that these compounds should delaminate in specific conditions. To our knowledge, this is the first attempt made to apply such approach to obtaining nanoparticles of rare-earth sulfides. For the first time we demonstrated that $KLnS_2$ nanoplates could be prepared by liquid exfoliation and remains stable in colloidal solutions. It is possible to make highly oriented films using these dispersions.

2. Materials and methods

2.1. Methods and apparatus

The x-ray powder diffraction (XRD) analysis of the samples was performed on a Shimadzu XRD7000 diffractometer (CuKα radiation, Ni filter, $2\theta = 10^\circ - 70^\circ$). Raman spectra were recorded with a Spex Triplemate spectrometer. UV spectra were recorded with UV-31101 PC Shimadzu spectrometer in the range 200–800 nm. Colloidal dispersions prepared by ultrasonic treatment were carried out in different solvents using ultrasonic bath "Sapphire," ultrasonic power 150 W, frequency 35 kHz. Centrifugation was performed on Janetzki T-32c centrifuge.

The DLS measurements were carried out in a 1 cm glass cuvette in a spectrometer NanoBrook Omni (Brookhaven Inst., USA). Scattering angle was 90°, for each measurement photon accumulation time was 10 s, the temperature was 20 °C (accuracy 0.1 °C). Autocorrelation was performed by spectrometer software with cumulant method for monomodal analysis and the NNLS (non-negatively constrained least squares) algorithm for polymodal analysis. Z-averaged (by intensity) hydrodynamic diameter D_h was calculated by Stokes-Einstein equation [36] for spherical particles. For all systems D_h were obtained by DLS monomodal and polymodal analyses. The solutions were measured without dedusting. Method error did not exceed 5%.

Atomic-force microscopy was carried on Solver Pro (NT-MDT) in tapping mode. Probe NGS30 (NT-MDT) (probe bend radius <10 nm, average force constant 40 N/m) was applied for sample scanning. Images were edited and analyzed using Image Analysis 3.5.0.2069 and ImageJ software [37]. The samples were prepared using several drops of diluted colloidal dispersions, which were applied to spinning at 2000 rpm silicone pieces and dried at an ambient temperature.

HRTEM micrographs were obtained by Cs-corrected transmission electron microscope Jeol JEM- 2200FS with point-image resolution 1.9 Å and acceleration voltage of 200 kV. Analysis of the local elemental composition (atomic%) was carried out using energy-dispersive EDX spectrometer.

2.2. Synthesis of Ln_2S_3

Samples of Ln_2S_3 were prepared by the chemical reaction of high-purity Ln_2O_3 as described in [38]. Reaction temperature was set 1000–1100 °C; reaction time varied for different Ln (from 1 h to La to 5 × 6 h for Lu, Yb). Process carried out until pure sulfide obtained, according to XRD pattern.