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Access to lanthanoid telluride nanoparticles: Liquid exfoliation of $LnTe_3$ ($Ln = La$, Ho)

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ABSTRACT

Although many of the nanoparticles containing lanthanoids are deeply investigated, the reports concerning chalcogenide materials are scarce. Comprehensive exploration of properties of these materials requires a proper preparation method avoiding hydrolysis and contamination with oxygen-containing products. Hence, in this case, the top-down approach could be preferable. In this study we demonstrated preparation of $LnTe_3$ ($Ln = La$, Ho) nanoparticles by liquid exfoliation method. Bulk tritellurides $LaTe_3$ and $HoTe_3$ afford stable dispersions in a number of common organic solvents under ultrasonic treatment. The size and morphology of nanoparticles in colloid solutions as well as films prepared from them were investigated by a number of methods (AFM, TEM, DLS, XRD, Raman). $LnTe_3$ form stable dispersions in alcoholic media with concentration up to 165 mg/L. In these dispersions nanoparticles exist as 1–2 layered charged flakes with lateral size 50–80 nm. The nanoparticles can be reassembled as films, which demonstrated orientation along $0k0$ direction.

1. Introduction

A great deal of attention has been focused on synthesis and characterization of 2D-materials, especially after discovering of graphene and its fascinating properties [1]. One of the most important families of 2D materials is the chalcogenide compounds with layered structure such as MoS_2, WS_2 [2,3], Bi_2Te_3 [4], NbS_3 [5], etc. Due to exotic electronic properties and high surface areas these materials are promising for catalysis [6,7], sensing [8,9], energy storage [10], and other applications.

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Among chalcogenides of different metals those of lanthanoid (Ln) elements demonstrate potential as high-temperature thermoelectric materials [11,12], solar energy conversion materials [13], pigments [14], infrared window materials [15], and phosphor host media [16]. Because of the high oxophility of lanthanoids synthesis of such nanoparticles remains a challenging problem. Conventional methods applied to other lanthanoid nanoparticles (sol-gel, spray-pyrolysis, hydrothermal, etc.) in case of chalcogenides can result in hydrolysis to oxygen-containing products. According to hard soft acid base theory (HSAB) [17], for hard ion Ln^{3+} it is more preferable to make bonds with hard ions (O^{2-}, F^-) than with much softer Q^{2-} ($Q^{2-} = S^{2-}$, Se^{2-}, Te^{2-}). While a large body of works about preparation, properties and application of various lanthanoid compounds were reported (e.g. nano-rare-earth oxides [18–21] and fluorides [22–24]) the number of studies describing nanostructured Ln chalcogenides are scarce. Preparation of EuS and EuSe was previously reported by a number of researchers [25–27]. There are only several studies of trivalent Ln sulfides [28–30] and a few examples of the selenides and tellurides [31–34].

For preparation of nanoparticles and 2D materials, a liquid exfoliation is one of the cheapest, fastest and effective methods [35].

Abbreviations: TMDC, transition metal dichalcogenides; DLS, dynamic light scattering; iPrOH, isopropyl alcohol; EtOH, ethanol; Py, pyridine; iAOH, isoamyl alcohol; NMF, *N*-methylformamide; DMF, dimethylformamide; NMP, *N*-methylpirrolidone

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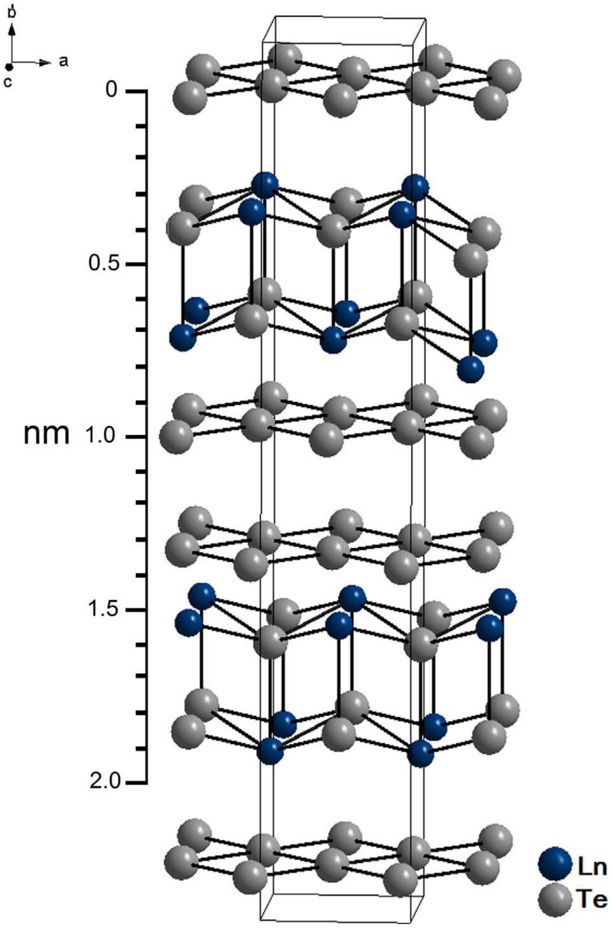

Fig. 1. Crystal structure of $LnTe_3$.

During this process, ultrasonic waves are applied to a mixture of bulk layered material and a properly selected solvent, providing enough energy to overcome the attraction forces between layers and generating exfoliated nanosheets. After sonication, the dispersion is centrifuged to remove particles that were not exfoliated. The result is a supernatant containing a colloidal suspension of material only a few layers thick. This approach was widely used for different layered materials with van der Waals gap in the structure as, e.g., transition metal dichalcogenides (TMDC) [36], BN [37] and graphene [38].

Among rare earth binary chalcogenides only LnQ_{2-x} (Q = S, Se, Te), Ln_2Te_5 and $LnTe_3$ possess layered structure. The latter compounds crystallize either in *Cmcm* or distorted *Ama2* orthorhombic structure composed of double layers of planar Te sheets separated by corrugated Ln_2Te_2 layers which are bonded by weak van der Waals interactions (Fig. 1). Such structure suggests that $LnTe_3$ can be exfoliated under appropriate conditions similarly to the TMDCs. Due to their structure and associated specific electronic structure, $LnTe_3$ has lately received significant attention as the first system in which nominal square-planar symmetry is broken by the formation of a unidirectional charge-density wave resulting in satellite reflections in diffraction characterization [39]. It is of great interest to examine these materials when the thickness of the crystal is limited by several nanometers.

To demonstrate applicability of this approach to different Ln, for our investigation we selected one light (cerium group) and one heavy (yttrium group) lanthanoids crystallizing in different space groups (Cmcm or Ama2 respectively). The latter structure exhibits elongation of the Ln-Te bond and a slight distortion of Te sheets while preserving the overall structure motif. In this report we present results of liquid exfoliation of $LaTe_3$ and $HoTe_3$ in different solvents as well as the study of their colloidal dispersions obtained by ultrasonication.

2. Materials and methods

2.1. Synthesis of $LnTe_3$

Compounds $LnTe_3$ (Ln = La, Ho) were prepared from stoichiometric mixtures of high-purity Ln and Te, with I_2 as mineralizer [40]. Samples were kept under inert atmosphere, as these compounds show noticeable change after several days of exposure to air.

0.472 g (3.4 mmol) of lanthanum and 1.302 g (10.2 mmol) of tellurium or 0.398 g (2.4 mmol) of holmium and 0.924 g (7.2 mmol) of tellurium was placed into a quartz tube. The tube was evacuated and filled with argon (repeated 3 times). 0.004 g (1.5×10^{-2} mmol) of iodine was placed into the tube filled with argon, then it was cooled in liquid nitrogen, evacuated and sealed. The tube was heated to 700 °C and held at this temperature for 72 h, then slowly (5 °C/h) cooled to 540 °C, after the heating was turned off. In both cases bronze-colored microcrystalline powders were obtained after reaction completion. The yields were quantitative: 1.772 g (99%) for $LaTe_3$ and 1.320 g (99%) for $HoTe_3$. There was no iodine in the obtained products according to EDS analysis.

2.2. Suspension preparation

Solvents were dried before use to remove residual water and to prevent possible hydrolysis of rare-earth telluride nanoparticles. Isopropanol (iPrOH) was distilled over Mg, acetonitrile over P_2O_5, ethanol (EtOH) over Na, pyridine (Py) over KOH, dimethylformamide (DMF) over BaO under low pressure and N-methyl pyrrolidone (NMP) over Na_2SO_4 under low pressure. Acetone was kept over molecular sieves 4 Å. Other solvents (isoamyl alcohol (iAOH), N-methylformamide (NMF)) were used as purchased. All solvents were deoxygenated prior to use by heating-cooling combined with argon bubbling. In a typical procedure of preparation of colloidal suspensions 10 mg of $LnTe_3$ and 10 mL of solvent was placed in glass flask, then again argon gas was bubbled through the liquid for 10 min, after that the flask was closed and sonicated using ultrasonic bath Sapphire (ultrasonic power 150 W, frequency 35 kHz) for 8 h in three times with a gap of 16 h. During ultrasonication, samples were termostated at 20–22 °C to prevent thermal restacking of colloidal particles. Resulting mixture was centrifuged for 10 min at 3000 rpm to sediment large particles, and upper 4/5 of supernatant solution were taken for further analysis. The colloidal dispersions were black or dark violet-brown at low concentration.

2.3. Preparation of films of colloidal dispersions

Films of the $LnTe_3$ were prepared to study their Raman spectra and X-ray diffraction. For this purpose 100–200 mL of the dispersion was filtered under low pressure through 'Vladipor' membrane filter with pore size of 50 nm.

2.4. Characterization

The X-ray powder diffraction (XRD) analysis of the samples was performed on a Shimadzu XRD7000 diffractometer (CuKα radiation, Ni filter, 2θ = 10°–70°). Raman spectra were recorded with a Spex Triplemate spectrometer. UV spectra were recorded with UV-3101 PC Shimadzu spectrometer in the range 200–800 nm. The infrared (IR) spectroscopy performed on a Scimitar FTS 2000 IR Fourier spectrometer. The samples were prepared as suspensions of powdered films in Nujol medium and measured between KBr windows. 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