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Synthesis of LaO_{0.5}F_{0.5}BiS_{2} nanosheets by ultrasonification

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LaO_{0.5}F_{0.5}BiS_{2} nanosheets were produced by ultrasonification. A slightly reddish colloidal suspension was obtained by ultrasonification of LaO_{0.5}F_{0.5}BiS_{2} powder in ethanol. Transmission electron microscope (TEM) images of the dried suspension indicated the nanosheet morphology of LaO_{0.5}F_{0.5}BiS_{2}, and the electron diffraction spots indicated 4-fold symmetry. The thickness of the sheets was 2–6 nm, which corresponded to 2–4 unit cells of the c-axis of LaO_{0.5}F_{0.5}BiS_{2}.

1. Introduction

Chalcogenite nanosheets, including MoS_{2}, WS_{2}, and ternary/quaternary compounds, have been extensively studied for use in catalysts, capacitors, sensing platforms, and so on. Ternary or higher nanosheets are particularly attractive since their properties can be tuned by controlling their chemical composition. Further study to explore new nanosheets can accelerate the development of new two-dimensional functional materials.

LnOBiS_{2} (Ln: La–Sm) species are layered mixed-anion compounds, the crystal structure of which is shown in Fig. 1. LaOBiS_{2} is a semiconductor with a direct band gap of ca. 1 eV; the bands near the Fermi level consist of Bi 6p and S 3p orbitals of Bi–S along the ab plane. Tuning the properties of LnOBiS_{2} by changing the anion sites has been reported. The doping of F into the O site increases the energy of the Fermi level, and F-doped LaOBiS_{2} thus exhibits metallic behavior and superconductivity below 3 K. Enhanced thermoelectric properties have reportedly been achieved by substitution of S for Se. Therefore, nanosheets of LnOBiS_{2} and related oxysulfides may prospectively exhibit various properties including light absorption, electronic conduction, or other unprecedented properties. Moreover, first-principles calculations predict that nanosheets of isostructural SrFBiS_{2} and BiOBiS_{2} should exhibit a large Rashba effect.

2. Experimental

LaO_{0.5}F_{0.5}BiS_{2} powders were synthesized by the solid-state reaction at 700 °C of mixed powders of La_{2}O_{3}, Bi, BiF_{3}, and Bi_{2}S_{3} in the nominal composition of LaO_{0.5}F_{0.5}BiS_{2}, according to the literature. A synthesized LaO_{0.5}F_{0.5}BiS_{2} pellet was ground with a mortar and pestle, and 0.1 g of the ground powder was placed in a centrifugal precipitation tube with 40 ml of ethanol. This tube was capped and ultrasonicated at 28 kHz for 60 min. The suspension was...
centrifuged for 20 min at 550 rpm and allowed to stand overnight. The top and middle portions of the liquid in the suspension were used for further characterization.

The crystal structure of the starting material was examined by X-ray diffraction (XRD; MiniFlex-600). The optical absorption of the suspension was measured using a V-670 UV–vis-NIR spectrophotometer. The morphology and electron diffraction images of the nanosheets were collected using transmission electron microscopy (TEM; JEM-2010). The thickness of the nanosheets was measured by atomic force microscopy (AFM; Nanocute). The nanosheets were affixed to the surface of a Si substrate by the dip-coating technique in conjunction with baking at ca. 80 °C.

3. Results

The XRD pattern (Fig. 2) of LaO$_{0.5}$F$_{0.5}$BiS$_2$ powder shows the diffraction peaks assigned as La O$_{0.5}$F$_{0.5}$BiS$_2$ [5]. The lattice parameters derived from 004 and 110 diffraction peaks were $a = 0.4068$ nm and $c = 1.337$ nm, which were close to the reported values ($a = 0.40527$ nm, $c = 1.33247$ nm [5]). Minor peaks of Bi metals were detected (Fig. 2).

Ultrasonification of LaO$_{0.5}$F$_{0.5}$BiS$_2$ powder in ethanol produced a transparent and slightly reddish suspension. The Tyndall effect was confirmed by passing a green laser beam through the solution, suggesting its colloidal nature (Fig. 3). Fig. 4 shows the optical absorption spectrum of the solution. The solution absorbs over a wide range of the visible spectral region, and a broad peak with a maximum at ca. 480 nm (blue absorption) was observed. This would include the optical absorption and scattering of the LaO$_{0.5}$F$_{0.5}$BiS$_2$ nanosheets.

Fig. 5 shows the TEM image of the synthesized sheets and corresponding electron diffraction pattern. The size of the nanosheet was approximately 300 nm. The electron diffraction spots indicated four-fold symmetry, which can be assigned to the diffraction of the $ab$-plane of the tetragonal structure of LaO$_{0.5}$F$_{0.5}$BiS$_2$. Notably, not all the particles observed by TEM analysis had sheet morphology; some particles were not thin enough to transmit the electron beam, and some particles had a tube-like shape; these were possibly produced by rolling the nanosheets. Energy dispersive X-ray spectroscopy shows peaks of La, O, F, Bi, S, which qualitatively agrees with LaO$_{0.5}$F$_{0.5}$BiS$_2$. 

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**Fig. 1.** Crystal structure of LaO$_{0.5}$F$_{0.5}$BiS$_2$: (a) view parallel to Bi–S layer and (b) perpendicular to Bi–S layer.

**Fig. 2.** XRD pattern of LaO$_{0.5}$F$_{0.5}$BiS$_2$ powder. Asterisk represent Bi metals.

**Fig. 3.** Suspension of LaO$_{0.5}$F$_{0.5}$BiS$_2$ nanosheets in ethanol. A green laser beam was passed through the suspension.

**Fig. 4.** Optical absorption spectrum of suspension of LaO$_{0.5}$F$_{0.5}$BiS$_2$ nanosheets in ethanol.

**Fig. 5.** TEM image of LaO$_{0.5}$F$_{0.5}$BiS$_2$ nanosheets and corresponding electron diffraction and energy dispersive X-ray spectroscopy spectrum.
Fig. 6. AFM image and height profile of LaO$_0.5$F$_0.5$BiS$_2$ nanosheets. Numbers indicate the positions for height profiles of the LaO$_0.5$F$_0.5$BiS$_2$ nanosheets.

Fig. 6 shows AFM images of the LaO$_0.5$F$_0.5$BiS$_2$ sheets on a Si substrate. The thickness of the sheet was 2–6 nm, which corresponded to 2–4 unit cells of the c-axis of LaO$_0.5$F$_0.5$BiS$_2$. Nanosheet assemblies with dimensions of a few tens of microns were observed. Although some aggregated particles were also found, these nanosheet assemblies suggested the potential for the formation of nanosheet films for device application.

4. Summary

The TEM and AFM results suggested that LaO$_0.5$F$_0.5$BiS$_2$ nanosheets were obtained by the ultrasonification route. As reported for many chalcogenide nanosheets [1], fabrication of the sulfide nanosheets, such as MoS$_2$ nanosheets, occurred by exfoliation due to the weak interaction between sulfur anions. In the case of LaO$_0.5$F$_0.5$BiS$_2$, exfoliation can be characterized by breakage of the interaction between the S anion and Bi cation having a lone pair. Further investigation of the synthesis route to achieve increased yield, control of the thickness and size of the nanosheets, as well as measurements of the nanosheet properties are underway.

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References