Nanotubes of (SmxY1-x)S-TaS2 based on Quaternary Misfit Layered Compounds (MLCs)

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Background including aims.
Misfit layered compounds (MLCs) have garnered considerable attention due to their fascinating chemistry and properties [1]. MLCs consist of two different layered oxides or chalcogenides that are stacked alternately along their c direction. The MLC stack is composed of metal chalcogenide (MX) which possesses a distorted rock salt structure and a transition metal dichalcogenide (TX2) which crystallizes in a hexagonal structure [1,2]. The properties of MLCs are determined by the chemical and structural interplay between MX and TX2. MLC-nanotubes (NTs) synthesized via the chemical vapor technique (CVT) offer potential applications in thermoelectrics due to the complementary properties of the two layered compounds [1]. Recently, a modified synthesis method of MLC-NTs has permitted the introduction of additional elements to form a quaternary compound starting from LaS-TaS2 [3,4]. Here, we present an in-depth electron microscopy analysis of the novel family of (SmxY1-x)S-TaS2 nanostructures [5]. In this novel family, the partial exchange of Sm(S) by Y(S) provides a pathway for the fine control of the MLC structure and its properties.

Methods
MLC-NTs made of (SmxY1-x)S-TaS2 were synthesized via the CVT technique [1-3] by varying the precursor proportions of Sm vs Y between x=0 to x=1. The samples will be designated by the Sm percentage, Sm20 corresponds to (Sm0.2Y0.8)S-TaS2 and similarly. To analyze these NTs, different TEM techniques (high-resolution (scanning)TEM (HR(S)TEM) imaging, selected area electron diffraction (SAED), electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS)) were performed. These TEM studies were developed using two aberration corrected Thermo Fisher Scientific Titan microscopes. Raman spectroscopy has also been employed to study these NTs.

Results
The detailed analysis of the NTs by electron microscopy and different spectroscopies verifies the partial substitution of Sm by Y in the (Sm,Y)S subsystem and also reveals the structural changes when compared to the pure SmS- or YS-TaS2 MLC-NTs. These structural changes can be linked to the slight difference in the lattice parameters of SmS and YS. Figure (a) corresponds to the SAED pattern of Sm40 (Sm0.4Y0.6)S-TaS2 sample where the reflections marked by the green dotted circles represent the reflections from (Sm,Y)S and reflections marked by red dotted circles represent the TaS2 subsystems, respectively. The c-axis periodicity (1.13 nm) is indicated by yellow arrows. The c-axis is perpendicular to the tube axis, which is given by the purple double arrow. A high-angle annular dark-field STEM image of a Sm80 NT is shown in Figure (b) and illustrates the repetitive layer stacking of (Sm,Y)S and TaS2. The inset of (b) shows a low-magnification TEM image of the Sm80 NT. Figure (c) depicts a Raman spectrum acquired from an individual Sm80 NT, which was fitted using a set of Lorentz functions. In a vibrational spectroscopy such as Raman, a Lorentz line shape is used to model pure vibrational modes, which only undergo homogeneous line broadening. Raman spectroscopy measurements of the whole set of samples reveal the tunability of the vibrational properties of these NTs. The study of the elemental composition of these NTs by

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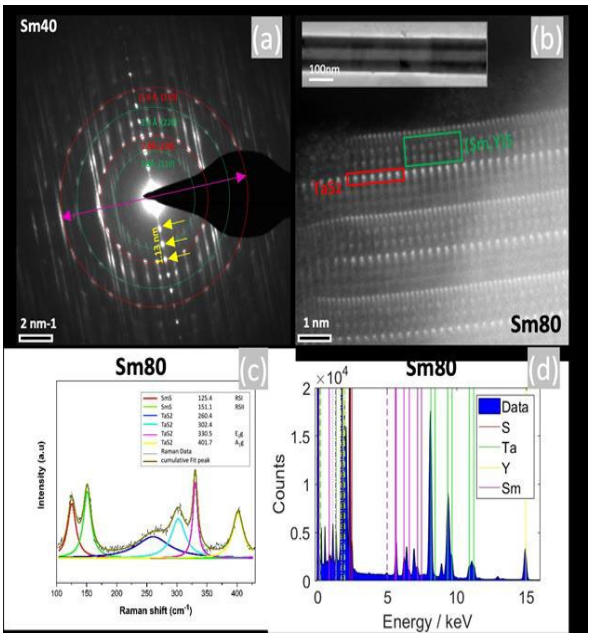
EDS is shown exemplary for a NT of the Sm80 sample in Fig 1(d), which reveals an average atomic weight percentage of around 17 at. % Ta, 24 at. % Sm+Y, and 59 at. % S. The EDS results obtained from all the samples show that the substitution of Sm by Y is homogeneous and in-phase with structural changes in the lattice parameter. Further low-loss EELS studies and electric properties of these samples are in progress. These investigations will also provide a more complete understanding of these systems including their electronic/optoelectronic properties.

Graphic:



Keywords:

Inorganic-nanotubes, misfit-layered compounds-(MLC), structural analysis

Reference:

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