



Synthesis of rock salt $\text{Pb}_{1-x}\text{Sr}_x\text{Te}$ with unusual stabilized compositions and their electrochemical performance

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ABSTRACT

The cubic crystal structure $\text{Pb}_{1-x}\text{Sr}_x\text{Te}$ polyhedral microcrystals with unusual stabilized compositions were synthesized using a facile solvothermal approach through balancing chemical reactivity of metal complex precursor and Te precursor. The presence of EDTA plays a crucial role in the formation of pure phase polyhedrons, avoiding the formation of SrCO_3 impurity. The various reaction kinetic experimental parameters, including proper metal complex precursors, mixed solvent ratios, the appropriate temperature, and the amount of KOH, were able to control the morphology of $\text{Pb}_{0.95}\text{Sr}_{0.05}\text{Te}$ and achieve much higher level of Sr alloyed into the PbTe matrix (5.2–6.5 mol% SrTe/PbTe), which is beyond its thermodynamic solubility limit of 1 mol% in bulk. Furthermore, these materials were successfully used as the electrodes of lithium ion batteries, possessing better cycling stability and the improved rate capability compared to pristine PbTe. We envision that the established strategy is general and robust, and offers easy access to other ternary PbTe-based alloy materials through careful balancing precursor chemical reactivity.

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1. Introduction

During the decades, attentions have been paid to the possibility of using the dimensional regime of micro- and nanomaterials as a tool to discover new materials. The stabilization of a new crystal form on the micro- and nanoscale for a composition which in the bulk adopts a different form (or does not even exist) is of fundamental interest in understanding the limits of phase stability as a function of size and in exploring the kinetics-thermodynamics balance. It is also an important new insight as to how new materials may be prepared that are unstable in the bulk but can be created uniquely on the micro- and nanoscale. Although stabilization of kinetic phases is quite challenging and uncommon, Kanatzidis's research group demonstrated the synthesis of semiconductor $\text{Pb}_{2-x}\text{Sn}_x\text{S}_2$ nanocrystals with a cubic rock salt crystal structure in a composition range where this structure is unstable in the bulk [1]. The $\text{Pb}_{2-x}\text{Sn}_x\text{S}_2$ nanocrystals are single phase solid solutions with cubic NaCl-type structure, which is a new class of materials. In addition, Hao et al. reported an exhaustive first-principles study of the atomic structure and thermodynamics

of ordering and phase stability in the ternary $\text{Sr}_x\text{Pb}_{1-x}\text{S}$ systems using density functional theory (DFT) and cluster expansion (CE) calculations [2]. They predicted and discovered the surprising existence of stable, ordered ternary compounds in the PbS-SrS system, which are previously unreported ordered rock salt-based compounds: SrPb_3S_4 , SrPbS_2 , and Sr_3PbS_4 . It should be emphasized that size reduction to micro- and nanoscale has impact on the crystal structure and property of the material.

Recently, Tian et al. showed that hole-doped samples of PbTe can be heavily alloyed with SrTe well beyond its thermodynamic solubility limit of 1 mol% using non-equilibrium processing [3]. Previous studies showed only a small equilibrium solid state solubility (less than 1 mol%) of SrTe in bulk PbTe [4,5]. Samples were prepared under thermodynamic control, using slow cooling procedures of molten mixtures (11 K h^{-1} from 1323 to 873 K), dissolving only very small amounts of SrTe. Although synthesis of inorganic solids using high-temperature method is a popular process, which generally leads to the formation of the thermodynamically stable product, it often leaves little room for kinetic modifications [6]. On the other hand, mild solution routes to synthesize PbTe-based ternary or quaternary micro- and nanocrystals tend to be more challenging as they can face the limitations of solubility of one or more of the precursors in a common solvent. At

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present, there are few reports about PbTe-based ternary or quaternary crystals through liquid phase methods. For instance, $\text{Pb}_m\text{Sb}_{2n}\text{Te}_{m+3n}$ and $\text{Pb}_m\text{Sb}_{2n}\text{Se}_{m+3n}$ nanocrystals have been successfully fabricated, which are new phases within the PbTe– Sb_2Te_3 and PbSe– Sb_2Se_3 system stabilized in the nanoscale regime [7,8]. In addition, a new phase of homologous $\text{Pb}_m\text{Bi}_{2n}\text{Te}_{3n+m}$ nanosheets were fabricated by Arindom Chatterjee et al. [9]. Recently, Fominikh et al. found that kinetic control enables the formation of thermodynamically less stable phases with increased solubility of the elements in mixed oxides. In their research work, highly dispersible $\text{Ni}_x\text{Co}_{1-x}\text{O}$ nanoparticles with rock salt type structure are obtained [10]. Similarly, in our previous research work, $\text{Pb}_m\text{Sb}_{2n}\text{Te}_{m+3n}$ and $\text{Pb}_m\text{Cu}_n\text{Te}_{m+3n}$ rock salt new phase micro/nanorods were prepared by two-step Te self-sacrificial template method [11,12]. However, to enhance solid solubility or form ordered new phases in solution route, despite decades of investigations in understanding the growth mechanism of semiconductor, the formation protocols of these multinary systems are not well known. Specially, ternary Pb–Sr–Te systems tend to be more challenging due to the limitations of solubility of one or more of the precursors in a common solvent. Chemical instability of Sr compound against oxidation upon air exposure and a lack of proper precursors of Sr^{2+} ions with suitable solubility have impeded the development of Pb–Sr–Te alloy in solution.

On the other hand, lithium ion batteries play an extremely important role in the fast-developing field of new energy. Lead has been studied as a potential anode material in lithium-ion batteries. Li–Pb alloy anodes have a theoretical capacity advantage over the commonly-used graphite, 582 mA h g^{-1} for Pb vs. 372 mA h g^{-1} for graphite. At present, various Pb-based compounds have been examined as materials for lithium-ion battery anodes, including Pb [13], PbO [14], PbSbO_2Cl [15], $\text{Pb}(\text{NO}_3)_2/\text{C}$ composite [16] and lead chalcogenides [17,18]. For instance, Chen et al. achieved over 200 mA h g^{-1} for 200 cycles with Pb-sandwiched nanoparticles [13]. Wang et al. reached a capacity of 250 mA h g^{-1} after 50 cycles with $\text{Pb}(\text{NO}_3)_2/\text{C}$ [16]. PbS nanoparticles performed poorly, with their capacity falling to 140 mA h g^{-1} after 100 cycles at a 1 C. Their poor performance was attributed to depletion of sulfur by polysulfide dissolution [17]. On the other hand, Te, a chalcogen group element, can also alloy with Li by forming Li_2Te (theoretical capacity for LIBs: 420 mA h g^{-1}). Recently, it is reported that PbTe has a potential use in low-power applications such as cell phones because PbTe nanoparticles cycled stably and maintained a capacity of 500 mA h g^{-1} after 100 cycles at 0.2 C and 300 mA h g^{-1} at a rate as high as 10 C [19]. Furthermore, Tu et al. found graphene-sandwiched PbTe nanoparticles were able to achieve capacities of 500 mA h g^{-1} that faded to 300 mA h g^{-1} after 100 cycles. However, bare PbTe performed poorly, with their capacity falling to 140 mA h g^{-1} after 100 cycles at 1 C [20]. Considering the electrochemical activity of Pb and Te with Li, they have high potentials as electrode materials for rechargeable Li-ion batteries. Furthermore, although the drawbacks of PbTe-based compounds such as the toxicity and environmental disposal/recycling problems restrict their practical application, it is still meaningful to probe electrochemical behavior of ternary lead telluride (PbM_xTe_y) from the viewpoint of basic scientific research. Besides the academic interest, the composition control of thermodynamically less stable phases can become an additional tool to tune the performance of materials in different energy-related fields [10]. To the best of our knowledge, although thermoelectric applications of PbTe-based compound have been widely reported, widely study on electrochemical properties of ternary PbTe-based compounds with rock salt structure remains rare so far.

Herein, we first reported a new phase $\text{Pb}_{1-x}\text{Sr}_x\text{Te}$ material, which synthesized through balancing chemical reactivity of Sr and

Pb precursor method in liquid route. It should be mentioned that the presence of EDTA plays an important role in the phase purity of product. Furthermore, their suitability as electrode materials in rechargeable Li-ion batteries with the intention of improving the capacity, stability, and rate capability of $\text{Pb}_{1-x}\text{Sr}_x\text{Te}$ materials were systematically investigated.

2. Experimental section

2.1. Synthesis

All the chemicals for the synthesis of $\text{Pb}_{1-x}\text{Sr}_x\text{Te}$ were used as obtained in this work without further purification. In a typical preparation process, first of all, 1.0 g KOH and 5 mL distilled water were put into a beaker. Then, 0.442 g (1.36 mmol) lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$) and 5 mL triethanolamine (TEA) was introduced into the above solution. After constantly stirring for 10 min and adding 0.3 g (1.12 mmol) strontium chloride (SrCl_2) and 1 g ethylenediaminetetraacetic acid disodium salt (EDTA), 0.32 g (1.44 mmol) sodium tellurite (Na_2TeO_3) and 0.5 mL concentrated hydrazine hydrate $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (80 wt%) were put into above solution. After being stirred for 15 min, the chemicals were good mixed. The resulting suspension was transferred into a 15 mL stainless Teflon-lined, kept heating at 180°C for 4 h and cooled to room temperature. Finally, the sample was washed by distilled water and ethanol for several times respectively, dried in a vacuum oven at 60°C for 6 h. The specimens were collected for analysis and characterization.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the products collected at room temperature were performed on a Rigaku D/max-2000 diffractometer equipped with Cu $K\alpha$ radiation from 20° to 80° with the step of 0.02° at scanning rate of 5 deg min^{-1} . The microstructure and composition analyses were conducted by a HITACHI SU 8000 field emission scanning electron microscope (FESEM) and energy-dispersive X-ray spectroscopy (EDX) implemented by FESEM was used to analyze the chemical compositions of the prepared products. The X-ray photoelectron spectra (XPS) of the products were collected with a Kratos AXIS ULTRA instrument, using Al- $K\alpha$ radiation as the excitation source. Additionally, infrared (IR) analysis of the products was performed with a FTIR spectrometer (Shi-madzu) in the range of $400\text{--}4000 \text{ cm}^{-1}$ in the form of KBr pellets.

2.3. Electrochemical measurements

The electrode was made of active material ($\text{Pb}_{1-x}\text{Sr}_x\text{Te}$ microcrystals), conductivity agent (Super P Li) and polymer binder (polyvinylidene difluoride, PVDF) in a weight ratio of 6:2:2, tape casted on a $200 \mu\text{m}$ thick copper foil, and dried at 100°C under vacuum for 12 h. The electrodes were incorporated into 2025 size coin-type cells with a solution of 1 M $\text{Li}[\text{PF}_6]$ in fluoroethylene carbonate (SolvayFluor)/diethyl carbonate (1:1w/w), Celgard 2400 separators, and a lithium foil counter electrode. Galvanostatic charge–discharge cycles of the cells were measured over potential ranging from 0.01 V to 2.5 V at current density of 1 C on a NEWARE CT-3008W cell test instrument. Cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) measurements were carried out with an electrochemical workstation (CHI600E), at a scan rate of 0.01 mV s^{-1} at 0.01–2.5 V and in a frequency range of 100 kHz to 0.01 Hz, respectively.

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