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Synthesis of nanocrystalline lead chalcogenides PbE (E = S, Se, or Te) from alkaline aqueous solutions

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Abstract

Reaction of a sulfur, selenium, or tellurium alkaline aqueous solution and $Pb(CH_3COO)_2{\cdot}3H_2O$ aqueous solution produces nanocrystalline lead chalcogenides PbE (E = S, Se, or Te) with a cubic phase at low temperature under atmospheric pressure. The products are characterized through X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) analysis. The average particle size is in the range 20–35 nm. The XPS analysis indicates that the stability of the product surface in air decreases in the order PbS, PbSe, and PbTe. An advantage of this synthesis method is that the PbE crystallizes well in the alkaline solution. The mechanism for the formation of the lead chalcogenides is discussed. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The investigations of IV-VI materials are stimulated by their extensive use in infrared optoelectronics for manufacturing IR lasers and detectors [1–5]. Heterostructures and superlattices have been attracting great interest for their fundamental electronic properties, which makes IV-VI materials quite competitive in device applications with other modern

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Table 1
Components of solutions A and B, and the lead chalcogenides resulting from their combination

Final product	Solution A	Solution B
PbS	0.005 mol elemental S in 50 ml NaOH (0.1 mol) aqueous solution	0.0051 mol $Pb(Ch_3COO)_2 \cdot 3H_2O$ in 5–10 ml distilled water
PbSe	0.0025 mol elemental Se in 50 ml NaOH (0.56 mol) aqueous solution	0.0026 mol $Pb(CH_3COO)_2 \cdot 3H_2O$ in 5–10 ml distilled water
PbTe	0.001 mol elemental Te in 50 ml KOH (1.20 mol) aqueous solution	0.0011 mol $Pb(CH_3COO)_2 \cdot 3H_2O$ in 5–10 ml distilled water

semiconductors [6]. These compounds are usually employed in the form of single crystals or epitaxial layers. However, over the past few years, the study of nanometer-sized crystallites has shown that the electronic structure of a semiconductor varies with particle size, and has provided the possibility of observing novel behavior, such as nonlinear optical effects and novel photochemical behavior [7,8]. Therefore, synthesis of semiconductor nanocrystallites has generated considerable interest.

Traditionally, PbE bulk materials have been prepared through the solid-state reaction of elements at elevated temperatures [9,10]. Organometallic precursors have also been used to obtain bulk powders and thin films of PbE at significantly lower temperatures (200–300°C) [11,12]. Rees et al. [13–15] have synthesized lead thiolates $Pb(SR)_2$, which can be converted into lead sulfide PbS by thermolysis. Low-energy approaches include the simple precipitation of metal chalcogenides from aqueous solutions of the metal cation [16], the arrested precipitation of micelles [17], and the trapping of metal chalcogenides within a polymer matrix [18] for the formation of controllable nanoparticulate chalcogenides. In the low energy routes, the toxic gas H_2E ($E = S$, Se, or Te) is often used as the chalcogen source. In recent studies, a nonaqueous solvent and elemental S, Se, or Te as the chalcogen source were used to synthesize metal chalcogenides. It has been reported that reactions of sulfur, selenium, or tellurium with elemental lead in *n*-butylamine at room temperature produces crystalline PbE ($E = S$, Se, or Te) [19]. Another report [20] demonstrates the synthesis of lead chalcogenides by a solvothermal method at 120–160°C, using toxic ethylenediamine as solvent [20].

The objective of this work was to find an aqueous solution route for preparing nanocrystalline lead chalcogenides. We chose to use elemental sulfur, selenium, and tellurium as the chalcogen sources, each dissolved in an alkaline aqueous solution, to prepare PbE ($E = S$, Se, or Te), because all crystallize well at low temperature under atmospheric pressure. The precursors and solvents are relatively simple and safe.

2. Experimental

First, solutions A and B, as described in Table 1, were prepared separately. Heating to boiling temperature can accelerate the dissolution of elemental S, Se, or Te in the alkaline