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Electronic transport study of PbSe pellets prepared from self-assembled 2D-PbSe nanostructures

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ABSTRACT

This work presents a study of the electronic transport properties of PbSe pellets fabricated starting of PbSe nanostructures that exhibited a flake-like 2D morphology, which were synthesized by the co-precipitation method. Seebeck coefficient measurements revealed that the PbSe sample displays n-type conductivity, a maximum Seebeck coefficient of −512.6 μV/K around 380 K, and that the carriers scattering is dominated by acoustic and optical phonons. The Fermi level dependence on the temperature and the band gap energy are also reported. Interestingly, size-dependent confinement effects due probably to the reminiscent PbSe 2D character could be evidenced.

1. Introduction

Semiconductor lead chalcogenides (PbS, PbSe and PbTe) are currently studied due to their singular physical properties: narrow band gap energy, relatively large Bohr exciton radius and positive temperature coefficient, which make them promising materials for the development of quantum effects-based energy conversion devices. Lead selenide (PbSe) crystallizes in the face-centered cubic structure of the rock-salt, with a lattice parameter of 6.121 Å, its band gap is about 0.28 eV at 300 K and it has a Bohr exciton radius as great as 46 nm. Additionally, it has been established that PbSe can display either n- or p-type conductivity, depending on the dominant point defect in its crystalline lattice. This material has successfully been tested as an absorbent material of multi-generation solar cells [1], communication devices [2], thermoelectric devices [3,4], FETs [5] and IR spectrum detectors [6].

Several techniques have been used to synthesize nanostructured PbSe, including ball-milling [7], chemical bath deposition [8,9], colloidal chemistry [10–12] and also solid-state reactions of elemental Pb and Se at high temperature [13]. Among this variety of synthesis methods, chemical co-precipitation in solution stands for an effective, facile and cheap route for growing nanocrystalline semiconductors at relatively low temperatures. Also, under specific conditions, co-precipitation allows for obtaining a variety of nanoscale semiconductors with extraordinary morphologies and enhanced properties that greatly differ from their bulk versions [14]. Additionally, the co-precipitation method is a well-adapted method to obtain larger, irregular and highly anisotropic nano- or micro-sized structures by oriented self-assembly [15,16].

For thermoelectric applications, nanostructured semiconductors hold promise to separately control the electrical and thermal transport and so produce improved-efficiency thermoelectric devices. For instance, the maximum Seebeck coefficients of a particular material for its both nano and bulk versions can display a difference as great as 100 μV/K [13,17]. Size-effect approaches to reach thermoelectric materials include quantum confinement of charge carriers [18], interface modification (superlattices and nano-heterostructures) [19–21] and doping modulation [22,23].

PbSe has unique properties by which the dimensionless figure of merit (*ZT*) might be improved using nearly nano-sized particles [22], since the confinement effects can be manifested for crystals less than 46 nm in size due to its relatively large Bohr exciton radius. Although the quantum confinement properties are interesting, transport processes are very relevant too, since the electrical conductivity, charge carrier mobility and Seebeck coefficient are

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controlled by the temperature, scattering processes and doping level in the samples. Therefore, it is mandatory characterizing the materials and to understand the main parameters related to already mentioned transport coefficients, and so to follow a suitable protocol to design high-efficiency thermoelectric devices later.

In this work, our early studies on the synthesis and electronic transport properties of as-synthesized nanostructured PbSe samples are reported. PbSe was synthesized at room temperature in water by a chemical route. Herein, we also present the morphology for these PbSe nanostructures. By means of thermoelectric measurements, it was found that as-synthesized PbSe exhibited n-type conductivity and high Seebeck coefficient. In addition, from those measurements, it was possible to extract the scattering coefficient, Fermi level position and magnitude of the band gap energy; these parameters are useful because they provide relevant information about the transport and the semiconducting behavior of PbSe samples.

2. Experimental details

2.1. Nanostructured PbSe synthesis procedure

In a previously published work, we described the synthesis procedure of nanostructured PbSe by co-precipitation. Briefly, using lead nitrate ($Pb(NO_3)_2$), ammonium hydroxide (NH_4OH), selenium powder (Se) as precursor sources and sodium borohydride ($NaBH_4$) as reducing agent for selenium. The lead and selenium precursor solutions were separately prepared by dissolving $Pb(NO_3)_2$ (2.25 mmol) and 16 ml of NH_4OH in 34 ml of deionized water on one side and by dissolving Se powders (2.25 mmol) and $NaBH_4$ (6.75 mmol) in 50 ml of water, and then they were heated at 70 °C under magnetic stirring in nitrogen atmosphere. Then, the synthesis reaction is performed by mixing the precursors under magnetic stirring in nitrogen atmosphere for 30 min, leading to the formation a black precipitate, comprising both of PbSe and reaction byproducts. Byproducts were removed from the reaction beaker by sequential rinsing and decanting steps, adding a 0.25 M HCl aqueous solution and deionized water. After five rinsing-decanting cycles pure PbSe was obtained, and then completely dried by lyophilization for overnight. The resultant PbSe powder was collected to form a PbSe pellet as described below.

2.2. PbSe pellet preparation

The obtained PbSe powders were transformed into a pellet as follows: 600 mg of PbSe powders were loaded into a stainless steel die, and then pressed into a disk-shaped pellet (12.75 mm in diameter and 1.1 mm thickness) at 384 MPa for 4 h under laboratory conditions. The as-prepared PbSe pellet was pre-annealed at 65 °C for 4 h to eliminate possible structural stress and cracking after the pressing. Finally, the pellet was subjected to a rapid thermal annealing at 130 °C for 20 min in vacuum to avoid the sample annealing during the thermoelectric measurements.

2.3. Sample characterization

Prior to the pellet fabrication, powdered PbSe was characterized in regards to its morphology using a JEOL JEM-2010 Transmission Electron Microscope (TEM), operating at 200 kV and with a 20 cm in camera length. Seebeck coefficient was measured directly on the pellet in the 302–423 K temperature range. The measurements were performed in a home-made system by the differential method [24]. The pellet was placed onto two 2.0 mm-separated metallic heater bars. Two stainless steel jacketed thermocouples were used both to register the temperature and thermo-voltage. The temperature gradient was established by means of a digital temperature controller, which supplied the suitable current to the heater to produce an uneven temperature increasing between the bars. The data were collected by a LABVIEW program, which is interfaced to a National Instruments USB-9162 A/D converter-amplifier and to a Keithley 6517B electrometer to acquire the temperature and thermo-voltage values, respectively. The measurements were repeated five times to ensure reproducibility.

3. Results and discussion

3.1. Morphological and structural characterization

We have developed a procedure to reproducibly prepare 2D-PbSe nanostructures, as reported in our previously published work [25]. As shown in Fig. 1, these nanostructures display a flake-like morphology with 28.3 nm in average size. In that work, it was also explained how this particular morphology was originated by an oriented self-assembly process from 7 to 8 nm in size single PbSe nanocrystals. Furthermore, the electron diffraction pattern (inset) corroborated the crystallization into the FCC structure for the PbSe powders as a single phase.

Fig. 2 shows the Seebeck coefficient (S) as a function of the temperature (T). The negative sign on S values indicates that the 2D-PbSe sample has n-type conductivity. It has been reported that both selenium vacancies and lead interstitials are donor native defects in PbSe [26]. We have assumed that the selenium vacancies can be responsible for the exhibited PbSe n-type conductivity, because its formation energy is 2.15 eV/defect, which is comparable with that for interstitial lead [27]. This structural defect could be generated during the synthesis procedure (deviation of the Pb:Se molar ratio) and also during the annealing treatment, since selenium is evaporated due to its high vapor pressure.

As described in the experimental section, the reported S-T data (Fig. 2) were obtained by averaging the S values measured five times. It was noted that for each temperature, S values differed at most by 6% between two successive measurements. This appears

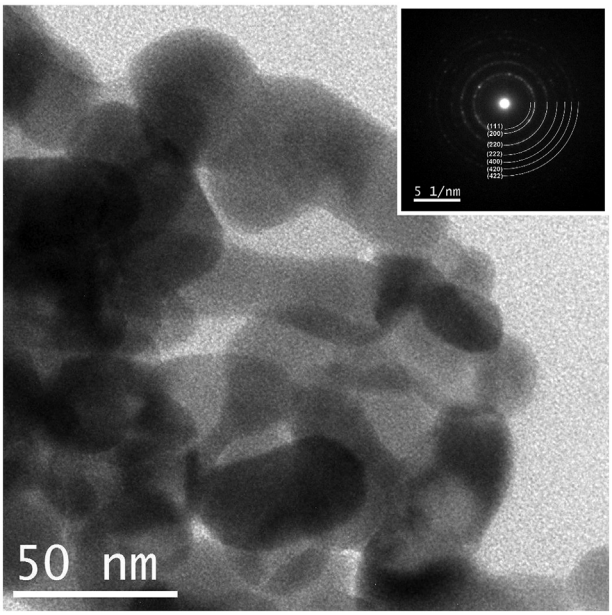

Fig. 1. TEM image of the PbSe nanostructures, the morphology is 2D nanoflake-like, arising from an oriented self-assembly process. Inset: electron diffraction pattern of the sample exhibits well-crystallized FCC structure as the unique phase.