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Electrical and thermoelectric properties of PbSe doped with Sm

M.M. Ibrahim, S.A. Saleh *, E.M.M. Ibrahim, A.M. Abdel Hakeem

Physics Department, Faculty of Science, Sohag University, Sohag, Egypt

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Abstract

The electrical conductivity (σ), Seebeck coefficient (S) and power factor ($S^2\sigma$) of $Pb_{1-x}Sm_xSe$ ($x = 0.00$, 0.03, 0.06 and 0.09) annealed at 215 °C for different time periods have been investigated in the temperature range of 90–450 K to explore the effect of Sm doping and time of annealing on the PbSe thermoelectric performance. The XRD analysis does not exhibit any deviation from the characterizing rock-salt structure with changing the Sm amount or annealing time. Increasing Sm content resulted in increasing the activation energy as the character of other magnetic dopants. The thermoelectric measurements show that all samples are n-type semiconductor and the modulus value of Seebeck coefficient increases with increasing Sm content from $x = 0.00$ to 0.06. The highest value of power factor 83.8 $\mu W\,cm^{-1}\,K^{-2}$ has been recorded for $Pb_{0.94}Sm_{0.06}Se$ sample annealed for 180 min. The results indicate that samarium can be introduced as a dopant for PbSe to enhance its thermoelectric performance.

Keywords: PbSe; Annealing; Thermoelectric materials; Power factor

1. Introduction

Lead chalcogenides have been involved in many applications. They have been used as sensors for infrared radiation, photoresistor, lasers, solar cells, optoelectronic devices and thermoelectric devices [1–9]. Thermoelectric devices have been used practically in wider areas recently, such as in consumer products like small refrigerators and in high-tech applications like in cooling units for fiber junctions in optical fiber communication technology [10,11]. They are reliable energy converters and have no noise or vibration, as there are no mechanical moving parts [12,13]. Also devices based on this technology can be manufactured at very small size, which enables application to very local area with precise temperature control [10–13].

There were interests to introduce PbSe compounds by many researchers as thermoelectric materials for cooling and power generation applications. The power factor (Pf) is a good monitor for the thermoelectric (TE) performance. Since it is given as $Pf = S^2\sigma$, where S is the Seebeck coefficient and σ is the electrical conductivity, it is carrier concentration dependant. Story [14] reported that IV–VI compounds allow for simple control of carrier concentration by means of doping and isothermal annealing. So, TE performance could be enhanced by optimizing both the doping and thermal treatment processes.

The effect of thermal treatment had been tested by many researchers [15–20]. For instance, Unuma et al. [18] measured the Seebeck coefficient and electrical conductivity in a temperature range from room temperature to 600 K in argon atmosphere for pressureless-sintered PbSe ceramics. The results implied changing in temperature dependence of thermoelectric power and electrical conductivity by changing the sintering conditions. They reported that, increasing the sintering temperature is associated with changing the Seebeck coefficient sign and reducing the conductivity by one or two orders of magnitude.

Many researchers reported that, doping IV–VI semiconductors with variable values of elements results in appearance of a range of unusual effects that are not characterizing the undoped material, [14,21,22]. In the past, only the group III elements (AL, Ga, In, and Tl) represented the impurities of IV–VI compounds. However in recent publications the impurities elements were expanded to include Cr, Yb, Eu, Gd, and Ce transition elements. Doping with these elements transforms IV–VI semiconductors into semimagnetic semiconductors [21–28]. In the other side, Skipetrov et al. [29] reported that ytterbium doping modifies the energy spectrum of charge carriers in lead telluride by formation of deep impurity level. At low Ytterbium content this deep level is resonant with the valence band, however by increasing the impurity concentration it approaches the valence

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* Corresponding author. Tel.: +20 104311140; fax: +20 934601159.
E-mail address: saleh2010_ahmed@yahoo.com (S.A. Saleh).

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band edge and shifts into the forbidden band. Also, the physical property of $Pb_{1-x}Eu_xSe$ is the rapid increase in the energy gap with increasing Eu content [10,30–32]. Another evidence for the influence of the doping process on the thermoelectric properties of IV–VI compounds was introduced by Su et al. [33]. They announced that for n-type lead telluride (PbTe) compounds doped with Sb_2Te_3, the electrical conductivity and the absolute value of Seebeck coefficient increase with increasing the Sb_2Te_3 content. The thermoelectric performance enhancement of PbTe in their study may be due to the high pressure under which the samples were prepared in addition to the low lattice thermal conductivity resulted from using Sb_2Te_3 as source of doping.

This work as a part of research plan [22] aims to introduce samarium as a dopant for PbSe compound and to optimize the doping level and thermal treatment conditions to obtain the best performance of $Pb_{1-x}Sm_xSe$ ($0 \leq x \leq 0.09$) as a thermoelectric material.

2. Experimental

The samples were prepared from high-purity (99.999%) elements obtained from Aldrich. The alloys were formed by direct melting the mixtures of the pure elements at 1100 °C in silica tube sealed under vacuum (10^{-5} Torr). The melting duration was 12 h with frequently agitation to ensure complete homogeneous mixing and it was followed with quenching in ice cold water. Then the quartz tube was broken and the ingots of the samples were grounded thoroughly for 2 h to obtain fine particles. This was ensured by sieving the powder by a sieve with apertures diameter equal to 63 μm. The powder of each composition was divided into equal amounts and pressed under 5 t/cm^2 to be in pellet form. The annealing process was performed at 215 °C for different time intervals 160, 180, 200, 220 and 240 min in vacuum controlled furnace. This temperature was chosen below the lowest invariant temperature of the constituent binary diagram of PbSe. The internal microstructure of the $Pb_{1-x}Sm_xSe$ ($x = 0$, 0.03, 0.06 and 0.09) system was characterized by X-ray diffraction (XRD) (Bucker Axs-D8 Advance diffractometer with Cu K_α radiation). The electrical and thermoelectric measurements have been carried out using especially made sample holder. Both of measurement processes were performed over temperature range 90–450 K in a vacuum 10^{-3} mmHg which was found to contribute much to the thermal stability during measurements. For the electrical measurements, a dry cell has been used as voltage source and the current was measured using Keithley's electrometer. The voltage in both types of measurements was measured using Keithley 182 sensitive digital voltmeter. The temperature of the specimen and temperature gradient in the thermoelectric measurement were sensed by standard copper-constantant thermocouples.

3. Results and discussion

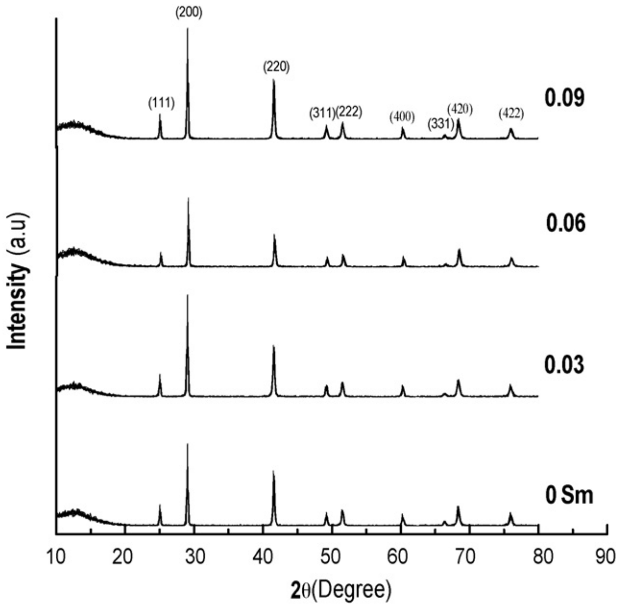

Fig. 1. XRD patterns of the alloys $Pb_{1-x}Sm_xSe$: (a) $x = 0.00$; (b) $x = 0.03$; (c) $x = 0.06$ and (d) $x = 0.09$.

The results of X-ray diffraction patterns are shown in Fig. 1. The *d* values are in good agreement with JCPDS data (see cart no. 6-354) confirming the rock salt (NaCl) structure of all the investigated samples [34–36]. In addition, the diffraction peaks corresponding to the ternary compounds of Pb_xSm_ySe are not found. This is expectable, because with Sm doping Pb^{2+} ions are substituted by Sm^{3+} ions [37] and the resultant SmSe system crystallizes also in NaCl structure [37,38]. The absence of the diffraction peaks corresponding to the ternary compounds matches well with Su et al. [33] whom pronounced that the ternary compounds of doped IV–VI compounds should not be formed with high cooling rate, small synthetic pressures and small dopant amounts which are the conditions of sample preparation in this work. Based on these results, the investigated samples are single phase PbSe while samarium is the source of dopant for PbSe. The presence of sharp structural peaks in the diffractograms suggests polycrystalline nature of the samples [36]. The appearance of the most prominent diffraction peak at 2θ equal to 29.2° which corresponds to (2 0 0) plane indicating the predominant growth of crystallites in this direction [36].

Electrical conductivity is a prominent factor which reveals reliable information about the transport phenomena. As it was mentioned above, the temperature dependence of electrical conductivity for the samples of $Pb_{1-x}Sm_xSe$ ($x = 0.00$, 0.03, 0.06 and 0.09) compositions annealed at 215 °C for 160, 180, 200, 220 and 240 min has been tested in the temperature range $90 \leq T \leq 450$ K. In Fig. 2 the temperature variations of the electrical conductivity exhibit the characteristic extrinsic behavior of PbSe compositions [39,40] where the conductivity decreases with increasing temperature, reaches its minimum value at certain temperature T_s and then increases. At low temperature ($T < T_s$), the electrical conductivity is a characteristic of extrinsic conduction, while at higher temperature ($T > T_s$) the number of carriers thermally excited across the semiconducting energy gap begins to overwhelm the number of carriers due to ionized impurities and the intrinsic conduction begins to predominate [41,42]. In the intrinsic semiconductor behavior region, the temperature dependence of electrical conductivity can be fitted to the relation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_\sigma}{k_B T}\right)$$

where σ_0 is the pre-experimental factor representing the temperature independent conductivity, and E_σ is the activation energy for conduction. The $\ln\sigma$ versus $1000/T$ plots in Fig. 3 are linear for all samples which confirm that the conduction in the concerned range of temperature is through thermally activated