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CHARACTERIZATION OF $PbSe_{1-x}Te_x$ SYNTHESIZED BY SOLID-STATE MICROWAVE PLASMA ASSISTED

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Polycrystalline $PbSe_{1-x}Te_x$ ingots were prepared by solid-state microwave synthesis, and their microstructure morphologies and stoichiometric ratio were examined using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). Polycrystalline thin films of $PbSe_{1-x}Te_x$ were then deposited onto clean glass substrates using vacuum evaporation technique at 10^{-6} mbar. X-ray diffraction (XRD) patterns indicated that the lattice constants of $PbSe_{1-x}Te_x$ powders and thin films increased with the increasing amount of Te, in accordance with Vegard's law. The electrical conductivity and thermoelectric power of the thin films were measured at a temperature range of 298–523 K. From the measurements of electrical properties, the thin films were characterized by n-type behavior, with carrier concentrations varying slightly with increasing Te.

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1. Introduction

In the past decades, PbSe and PbTe materials have attracted considerable attention as potential devices in thermoelectric (TE) power applications. The performance of solid-state TE device is greatly determined by the magnitude of the figure-of- merit, ZT. This is given as $ZT = S^2\sigma T/K$, where S is the Seebeck coefficient or thermal power, σ is the electrical conductivity, K is the thermal conductivity, and T is the absolute temperature of the given TE material. The power factor ($S^2\sigma$) study, which states that ZT may be enhanced by reducing K and increasing σ, is among the significant studies that aim to determine the behavior of materials for TE devices [1]. The electrical conductivity is mainly decided by the electronic band structure, which can be improved through appropriate chemical doping. Phonon transportation is mainly responsible for the thermal conductivity in semiconductor-based TE materials [2]. According to another study, PbSe and PbTe may be prepared using the newly developed technique of solid-state microwave synthesis [3]. Interestingly, compounds prepared using solid-state microwave synthesis may possess improved physical properties compared with compounds synthesized using other techniques [4]. To the best of our knowledge, no prior reports have measured the thermoelectric properties of a mixture with PbSe and PbTe, such as $PbSe_{1-x}Te_x$, which is prepared using solid-state microwave synthesis. In recent years, there has been growing interest on the composition of $PbSe_{1-x}Te_x$ materials due to their ability to combine the advantages of the two end materials [5]. In the present study, we first prepared PbSe, PbTe, and $PbSe_{1-x}Te_x$ ingots by solid-state microwave synthesis. Afterwards, we studied the structural and thermoelectric properties of its thin films at 300 K.

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2. Experimental

In the present study, solid state microwave synthesis was used to prepare the ternary polycrystalline ingots of $PbSe_{1-x}Te_x$ alloys. A total of 2 g of Pb, Se, and Te elements of high purity powder (> 99.999% 100 mesh) were weighed using an electronic balance, in accordance with the stoichiometric ratio of 1:(1-x):x, respectively. The mixture was then transferred to an agate mortar and pestle and ground for 20 minutes. The mixture was placed in a 12 mm (O.D.) × 10 mm (I.D.) quartz ampoule and sealed after being evacuated at 10^{-5} mbar. For about 25 minutes, the ampoule was exposed to microwave energy operating at 2.54 GHz, with maximum power of 800 W inside a cavity microwave oven (MS2147C 800 W). The reaction time was recorded, and the mixture was shaken every 5 minutes. During the timed reaction, $PbSe_{1-x}Te_x$ compound flashed blue upon completion of the configuration of the composite. Then, $PbSe_{1-x}Te_x$ ingots were examined using SEM and (EDX) (JSM-6460 LV). The polycrystalline thin films of $PbSe_{1-x}Te_x$ were then deposited onto clean glass substrates by thermal evaporation at 10^{-6} mbar using an Alcatel-101. The ground powder and thin films were measured by XRD (PANalytical X'Pert PRO MRD PW3040). The electrical conductivity and thermoelectric power were measured at a temperate range of 298–523 K. The Hall voltage was measured using the Vander Paw method at 300 K. The thickness of the thin films, which were measured using Filmatric F20, was 158±6 nm.

3. Results and Discussion

The phase compositions of the powders and thin films of $PbSe_{1-x}Te_x$ samples were examined using XRD spectra. The results are shown in Fig. 1a and 1b. All the samples were single-phase and have rock salt (NaCl) structure with a dominant peak representing the plane (200) of $PbSe_{1-x}Te_x$, and display an apparent shift to high angle with increasing the tellurium content, which is mainly due to the larger atomic radius of tellurium (1.4 Å) compared with that of selenium atom (1.15 Å), presumably verifies that the tellurium atoms successfully enter into the lattice structures of $PbSe_{1-x}Te_x$. The spectra were consistent with those of the JCPDS card files (No. 06-0354 and 38-1435). The cubic lattice constant a was calculated using the following equation [6]:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad . \tag{1}$$

Table 1 shows the respective lattice constants of $PbSe_{1-x}Te_x$ powders and thin films for different values of x. The lattice constants for both increased linearly as concentration x increased. Therefore, the lattice constant variation followed Vegard's law [7]. The average crystallite size, obtained using Scherrer's formula based on the XRD patterns [6]

$$D = \frac{0.9\lambda}{\beta Cos\theta_B} \tag{2}$$

where D is the average crystalline (grain) size, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of XRD peaks and θ_B is the Bragg angle, the grain size remains almost constant at 416–417 Å with increase in Te content from *x* = 0.0 to *x* = 1.0, while decreased at 413 Å for both *x* = 0.2 and 0.4 in as-grown films.

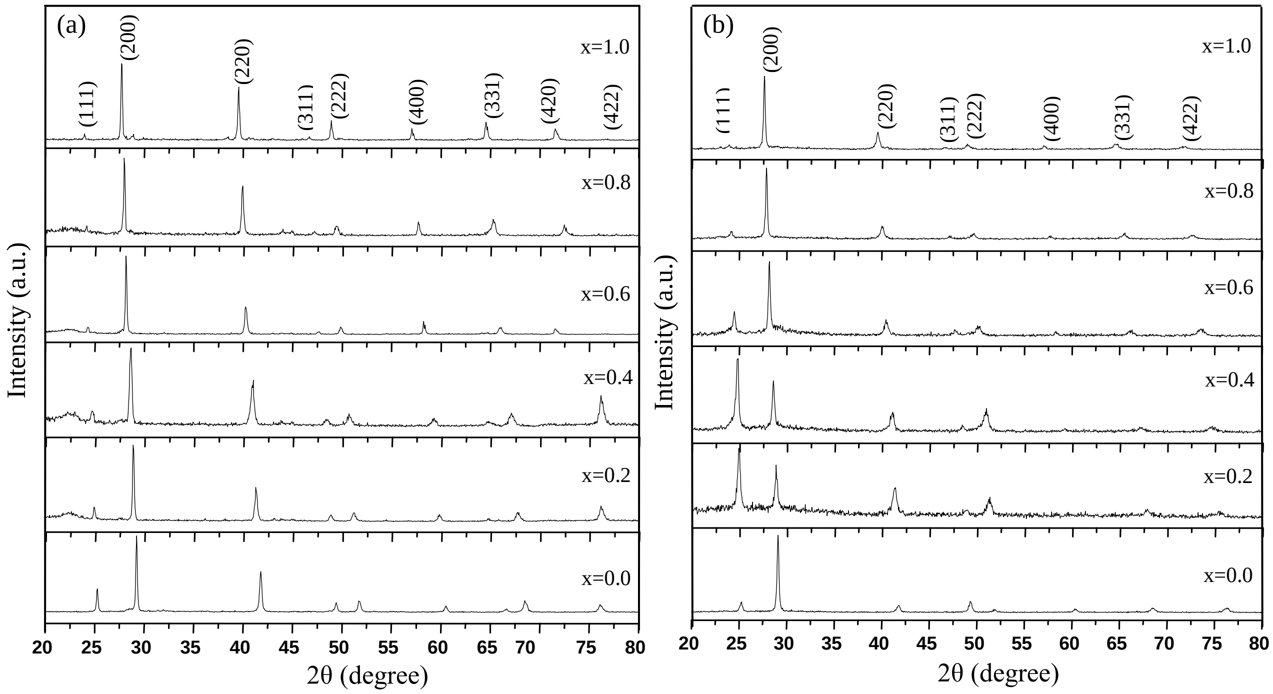

Fig 1- XRD of $PbSe_{1-x}Te_x$ alloys in the form of (a) powders and (b) thin films.

SEM of PbTe ingot revealed the formation of micro-rods and cuboidal-shaped tubes, whereas other compositions showed the morphology of closely irregular plates, as shown in Fig. 2a. Thin films of $PbSe_{1-x}Te_x$ deposited at room temperature have a shiny and very smooth surface like mirror and there is high crystalline. The morphology on surface of the film was revealed the formation of nano-cubic crystallites was formed during the deposition. Effect of Te content on morphology of polycrystalline films is clearly evident in Fig. 2b, with the increase of Te content; surface diffusion and agglomeration of adatoms were enhanced. In addition, EDX spectra showed that the chemical composition analysis, it is concluded that the amount of Te, is substituted for Se stoichiometric ratio of the ingots $PbSe_{1-x}Te_x$ was near to the standard elemental weight, as shown in Table 1.

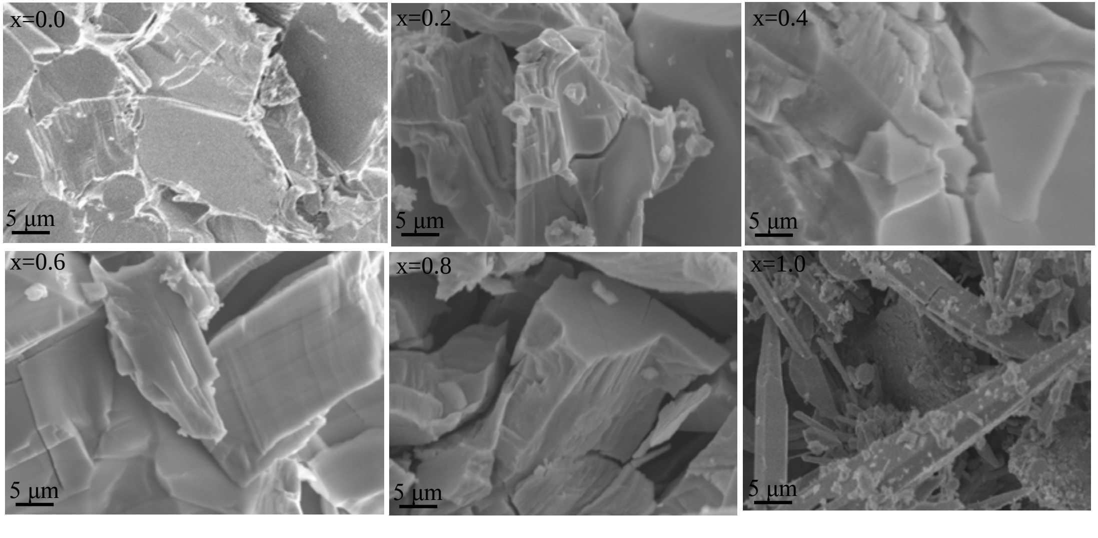

Fig 2 (a)- SEM images of $PbSe_{1-x}Te_x$ ingots.

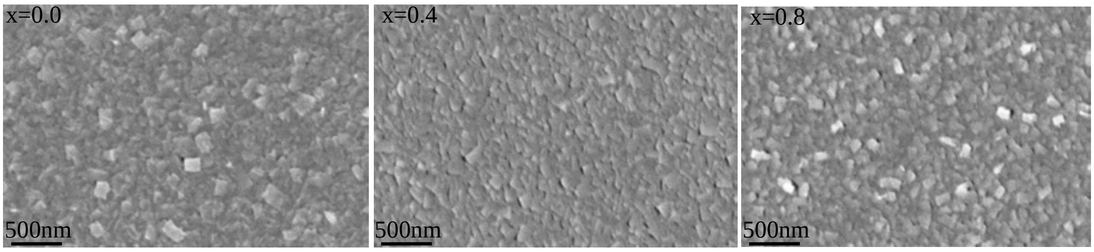

Fig 2 (b)- SEM images of PbSe$_{1-x}$Te$_x$ thin films 10KV, X30.000.

The electrical conductivity of all alloy thin films increased with increasing temperature, indicating the semiconductor behavior of all alloys. The variation of lnσ versus 1/*T* for six typical PbSe$_{1-x}$Te$_x$ films is shown in Fig. 3. It is evident from these curves that, in the case of PbSe$_{1-x}$Te$_x$, the conduction by thermally activated has two different mechanisms with two different slopes, that's mean obtained on two activation energies. The activation energy ΔE_a can be estimated from the plot of lnσ against 1/*T* according to the equation [8].

$$\sigma = \sigma_o \exp\left(-\Delta E_a/kT\right) \qquad (3)$$

where σ_0 is a parameter depending on the semiconductor nature, ΔE_a is the activation energy for electrical conduction and *k* is the Boltzmann constant. The electrical conductivity generally increases with increasing Te concentration.

Table 1- The structural and EDX parameters of PbSe$_{1-x}$Te$_x$ alloys at 300 K.

x content	Lattice constant (Å) Powder	Lattice constant (Å) Films	Volume of unit cube (Å) Films	Pb%	Se%	Te%
0	6.121	6.133	231.928	74.59	25.41	----
0.2	6.190	6.186	236.717	69.02	23.20	7.78
0.4	6.247	6.256	244.844	63.78	14.73	21.49
0.6	6.331	6.336	254.358	62.25	8.17	29.59
0.8	6.395	6.400	262.144	61.28	3.93	34.79
1	6.438	6.464	270.087	55.89	----	44.11

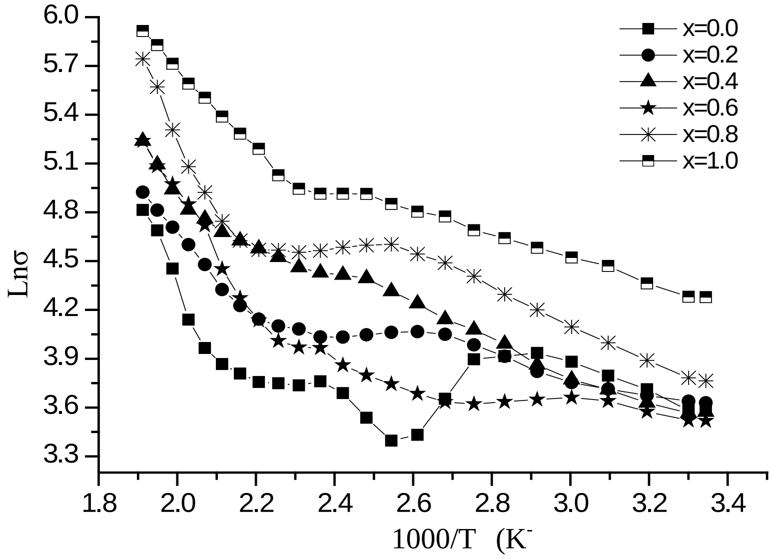

Fig 3- Plot of the logarithm of electrical conductivity versus 1000/T for PbSe$_{1-x}$Te$_x$ thin films.

The first electronic transition is in the low-temperature region of 300−383 K, whereas the other transition is in the high-temperature region of 443−523 K, indicating that a transition occurred near 383 K. The obtained values of ΔE_a at different Te content (x) for the $PbSe_{1-x}Te_x$ thin films have been shown in Table 2. The carrier concentration at room temperature is obtained from the Hall coefficient using equation $R_H=1/ne$, where R_H is the Hall coefficient and n is the carrier concentration. The carrier concentration decreased with increasing Te content and then increased at $x = 0.4$−1.0, which is similar to that of the doped content. The Hall mobility can be calculated from the carrier concentration and the electrical conductivity according to $\sigma = ne\mu$ (e = electron charge). The mobility decreased with the increase in proportion of Te, while x=0.2 and 0.1 increased depending on the Hall coefficient and electrical conductivity of the thin films (Table 2).

Table 2- Electrical conductivity (σ), Seebeck coefficient (S), Hall coefficient (R_H), carrier concentration (n), Mobility (μ) at 300 K, activation energy (ΔE) at 298−523 K.

Te content	Conductivity (S/cm)	Seebeck Coefficient (μV/K)	Hall coefficient (cm^3/C)	Carrier concentration (cm^{-3}) $\times 10^{17}$	Mobility ($cm^2/V.s$)	ΔE_1 (eV)	ΔE_2 (eV)
0	35.9	-189	-22.33	-2.79	801.647	0.255	0.595
0.2	38.03	-139	-24.86	-2.51	945.42	0.084	0.235
0.4	35.38	-103	-20.44	-3.06	723.16	0.09	0.308
0.6	33.79	-60.36	-20.78	-3.01	702.15	0.092	0.343
0.8	43.91	-93.46	-13.01	-4.80	571.27	0.096	0.541
1	72.31	-88.84	-12.97	-4.82	937.86	0.065	0.214

Similar behavior applies to the Seebeck coefficient S=ΔV/ΔT of the analyzed films was negative within the entire temperature range, indicating that the *n*-type (electron) carriers dominated the thermoelectric transport (Fig. 4). The behavior of the opposite applies to the Seebeck coefficient of the electrical conductivity of analyzed films, where decreases Seeback coefficient with increasing Te content. The power factors ($S^2\sigma$) exhibited a behavior typical of semiconductors, and increased with temperature of $PbSe_{1-x}Te_x$ compounds as shown in Fig. 5. It can be observed that the compounds with lower Te content (x=0.2) show very low power factor, while the compositions for x = 0.6, 0.8, and 1.0 have higher values. On the contrary, due to the high proportion of covalent bond component and thus high carrier mobility, the compounds with higher tellurium exhibits relatively better electrical conductivity and may be promising candidates for thermoelectric device.

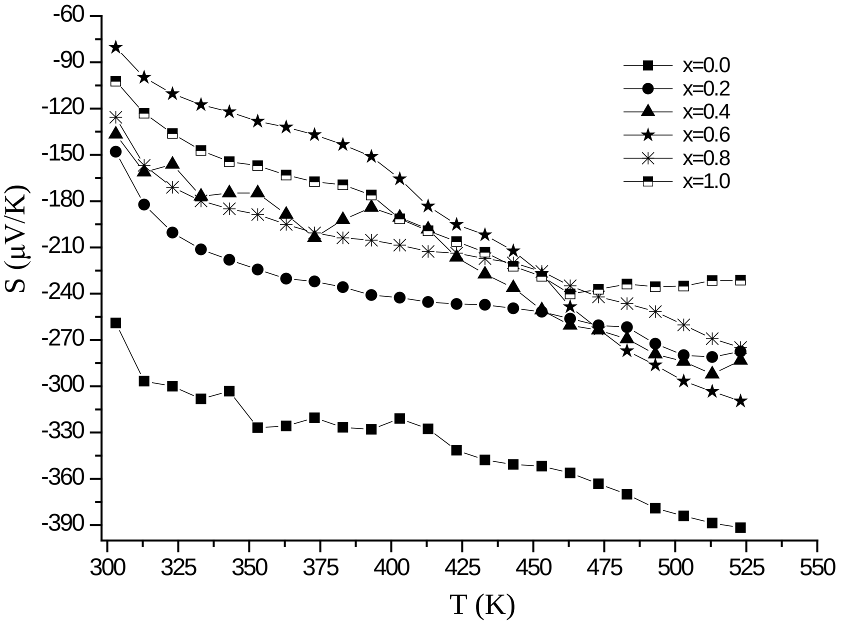

Fig 4- The Seebeck coefficient as a function of temperature for $PbSe_{1-x}Te_x$ thin films.

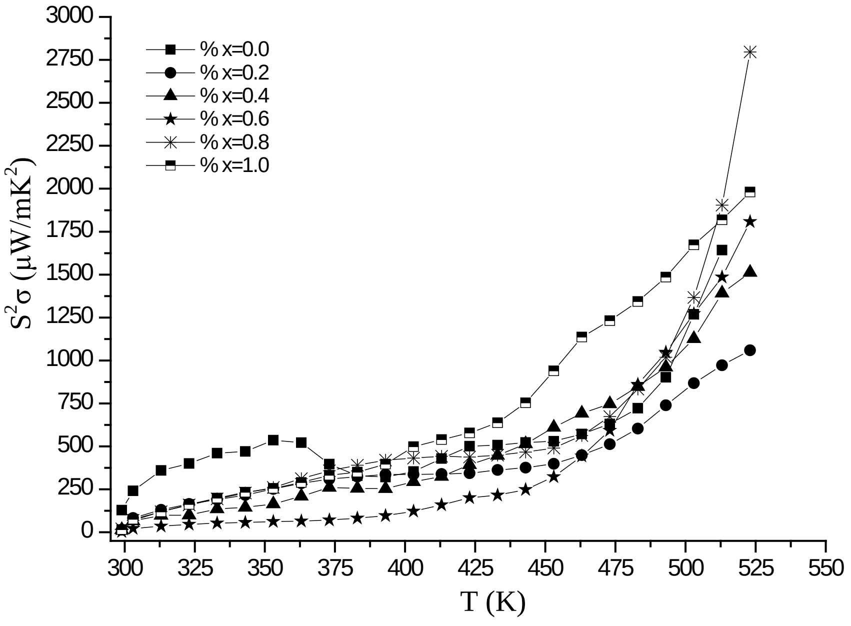

Fig 5- The power factor as a function of temperature for $PbSe_{1-x}Te_x$ thin films.

4. Conclusions

The ternary alloys of the microstructure $PbSe_{1-x}Te_x$ were successfully produced by solid-state microwave synthesis after 25 minutes of irradiation. The lattice parameter of the cubic unit cell increased with increased concentration of Te for the ground powders and thin films of $PbSe_{1-}$

$_x$Te$_x$. All the samples of PbSe$_{1-x}$Te$_x$ have pure-phase a rock salt (NaCl) structure with a dominant peak representing the plane (200), and display an apparent shift to high angle with increasing the tellurium content. The electrical conductivity and activation energy have been investigated. The conduction process in these films is through thermally activated process. On the basis of the measurements of the thermoelectric properties, we conclude that the power factor increased as tellurium content was increased to PbSe$_{0.2}$Te$_{0.8}$.

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