Journal of Alloys and Compounds 488 (2009) 334–338

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Influence of sulfur, selenium and tellurium doping on optical, electrical and structural properties of thin films of lead salts

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ARTICLE INFO

Article history:
Received 7 July 2009
Received in revised form 23 August 2009
Accepted 25 August 2009
Available online 31 August 2009

PACS:
71.20.Nr
72.15.Eb
73.61−r
78.20.−e

Keywords:
Lead chalcogenides
Band gap
Electrical conductivity
Lattice constant

ABSTRACT

Lead salts and their alloys with detecting and lasing capabilities have technological importance. High quality polycrystalline thin films of undoped and doped lead salts have been deposited by vacuum evaporation technique onto ultra clean glass substrates. Influence of sulfur, selenium and tellurium doping on optical, electrical and structural properties of lead salts has been investigated. Absorption coefficient and band gap of films were determined by absorbance measurements in wavelength range 2500–5000 nm using FTIR spectrophotometer. Dark dc electrical conductivity and activation energy of films were measured in temperature range 300–380 K through *I–V* measurements. Crystal structure and lattice parameters of films were determined from X-ray diffraction patterns.

1. Introduction

Semiconducting cadmium, lead, gallium and indium chalcogenides and their solid solutions are technologically important materials for micro- and optoelectronics of the new generation. The most interesting materials are chalcogenide solid solutions because changing their composition can alter the band gap width and consequently all their optical and electrical properties. Lead chalcogenides are one of the basic materials of modern infrared optoelectronics. Commercial lead salt detectors in the form of sensitized polycrystalline films have been widely used [1].

Narrow band gap and high carrier mobilities identify lead chalcogenides as basic materials for infrared optoelectronic devices [2] and thermoelectric materials in two-dimensional quantum well systems [3]. Narrow gap infrared focal plane arrays in two dimensions are fabricated for various applications. Preferred materials are HgCdTe and InSb. Narrow gap lead chalcogenides (PbSnX, PbEuX, where X = Se, Te) may be applied for this purpose. Photovoltaic lead chalcogenides sensors are rather tolerant to structural defects in contrast to HgCdTe and InSb material families [4].

Lead chalcogenides have been used as sensors for infrared radiation, photoresistors, lasers, solar cells, optoelectronic devices and thermoelectric devices [5–10]. Thermoelectric devices have been used in broad areas such as in consumer products like small refrigerators and in cooling units for fiber junctions in optical fiber communication technology [11,12].

The development of laser technology has opened up new applications for IV–VI compounds. The laser diodes based on lead chalcogenides and their alloys are important sources for the tunable radiations in the mid-infrared wavelength region. They are considered to be mainly utilized to an advanced measurement system for detecting hydrocarbon pollutants in atmosphere, high resolution spectroscopy, trace gas analysis and also to a new optical fiber communication system over super long distances [13–15].

Doping is one of the main tools for tuning free carrier concentration in semiconductors. Several researchers reported that the doping of IV–VI semiconductors with variable amount of elements results in the appearance of a range of unusual effects that were not characterizing the undoped materials [16–18]. The influence of concentration of impurities and doping process on the optical,

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doi:10.1016/j.jallcom.2009.08.126

electrical and structural properties of IV–VI compounds was investigated by various researchers [19–23].

In this work, attempts were made to optimize the parameters to obtain good quality films. The influence of sulfur, selenium and tellurium doping on optical, electrical and structural properties of thin films of lead salts (PbS, PbSe and PbTe) has been studied.

2. Experimental details

Melt-quenching technique has been employed to prepare polycrystalline bulk materials of undoped and doped lead salts. Highly pure materials 99.999% having desired compositional ratio of elements were sealed in quartz ampoules (length ~12 cm, internal diameter ~1 cm) in a vacuum of the order of 10^{-6} torr. Sealed ampoules were kept inside a programmable furnace where the temperature was raised up to 900 °C at a rate of 5 °C/min and then maintained it for 8 h. Ampoules were rocked frequently to ensure the homogenization of the melt. Ampoules having the material in molten state (stoichiometric melt) were allowed to cool down to room temperature. Ingots of samples were taken out and grinded into fine powder. Polycrystalline nature of samples was confirmed by X-ray diffraction patterns. Good quality polycrystalline thin films of thickness ~600 nm were deposited by vacuum evaporation technique onto ultra clean glass substrates kept at room temperature in a vacuum of the order of 10^{-6} torr. Deposited films were annealed in the same vacuum chamber at about 100 °C for 2 h and remain inside the vacuum chamber for 24 h to attain thermodynamic equilibrium as suggested by Abkowitz [24]. Thickness of films has been measured using quartz crystal thickness monitor. Deposition parameters were kept same for all films.

Absorbance spectra of thin films of undoped and doped lead salts were measured in wavelength range 2500–5000 nm using Fourier transform infrared spectrophotometer (Nicolet, Impact, model 410). For electrical conductivity, narrow films were deposited on glass substrates on which indium electrodes with narrow gap were pre-deposited. Dc conductivity of thin films was measured in temperature range 300–380 K. Electrical measurements have been carried out in a vacuum of 10^{-3} torr in a specially designed sample holder. For low field measurements, a dc voltage source in the form of a dry cell of 1.5 V has been used. Temperature of films was measured by a copper-constantan thermocouple and was increased by a step value of 2.5 °C and correspondingly the current was measured by an electrometer (Keithley, model 617). X-ray diffractometer (Philips PW 1140/09) was employed for studying the structure of thin films. The copper target was used as a source of X-rays with $\lambda = 1.5405$ Å (Cu Kα_1). Scanning angle was in the range of 10–90°. Scan speed of 2°/min was maintained.

3. Results and discussion

3.1. Optical characterization

Absorbance spectra of thin films of undoped and doped lead salts were studied to evaluate the absorption coefficient (α) and band gap (E_g). Absorption coefficient can be derived from the absorbance A, which is the ratio I_0/I_t, where I_0 is the incident intensity and I_t is the intensity after traversing a thickness t in the sample.

Absorption coefficient = optical density/thickness [25,26] or

$$\alpha = \left(\frac{1}{t}\right) \log\left(\frac{I_0}{I_t}\right) \tag{1}$$

The various types of transitions give rise to different frequency dependencies of absorption coefficient near the fundamental absorption edge. Absorption coefficient can also be given by [27,28]:

$$\alpha(h\nu) = A * (h\nu - E_g)^m \ \mathrm{cm}^{-1} \tag{2}$$

For allowed direct transitions $m = 1/2$ and A^* is constant. $h\nu$ and E_g being expressed in eV. Plotting $(\alpha h\nu)^2$ along ordinate axis and $h\nu$ along abscissa, we obtained straight line whose intercept on abscissa is equal to the forbidden bandwidth of sample. In case of lead salts the maxima of valence band and the minima of conduction band lie at the same k value of E–k band diagram and hence the transitions are direct type.

It has been observed that the absorption coefficient is high (~10^4 cm^{-1}) and increases sharply below a certain wavelength, for all the samples. Near the fundamental absorption edge, the absorption coefficient varies rapidly with wavelength. The variation of $(\alpha h\nu)^2$ with $h\nu$ for undoped and doped lead salts films is shown in Fig. 1(a–c). It has been observed that the plots of $(\alpha h\nu)^2$ versus $h\nu$ are linear over a wide range of photon energies indicating the direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the energy band gaps. The compositional dependence of the band gap is given in Table 1.

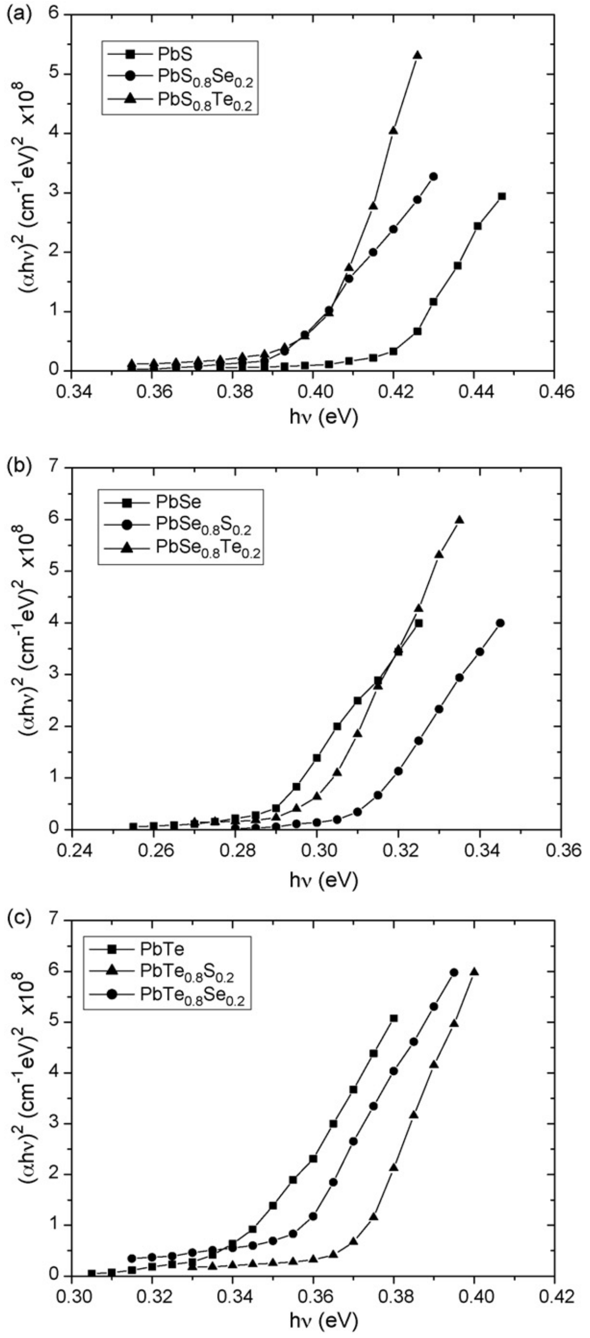

Fig. 1. (a) $(\alpha h\nu)^2$ versus $h\nu$ plot for PbS, $PbS_{0.8}Se_{0.2}$ and $PbS_{0.8}Te_{0.2}$. (b) $(\alpha h\nu)^2$ versus $h\nu$ plot for PbSe, $PbSe_{0.8}S_{0.2}$ and $PbSe_{0.8}Te_{0.2}$. (c) $(\alpha h\nu)^2$ versus $h\nu$ plot for PbTe, $PbTe_{0.8}S_{0.2}$ and $PbTe_{0.8}Se_{0.2}$.

3.2. Electrical characterization

Conductivity is an important factor which reveals the important and reliable information about the transport phenomenon of

Table 1
Optical, structural and electrical parameters of some compounds/alloys.

Compound/alloy	E_g (eV)	a (Å)	d (Å)	σ_{dc} (T = 345 K) (Ω^{-1} cm^{-1})	ΔE (eV)
PbS	0.42	5.95	2.98	0.001	0.18
$PbS_{0.8}Se_{0.2}$	0.39	5.97	2.91	0.012	0.13
$PbS_{0.8}Te_{0.2}$	0.40	6.04	3.02	0.038	0.14
PbSe	0.29	6.11	3.06	0.051	0.14
$PbSe_{0.8}S_{0.2}$	0.31	6.09	3.05	0.048	0.12
$PbSe_{0.8}Te_{0.2}$	0.30	6.18	3.09	0.066	0.11
PbTe	0.34	6.47	3.24	0.225	0.11
$PbTe_{0.8}S_{0.2}$	0.37	6.33	3.17	0.169	0.08
$PbTe_{0.8}Se_{0.2}$	0.35	6.40	3.20	0.147	0.10

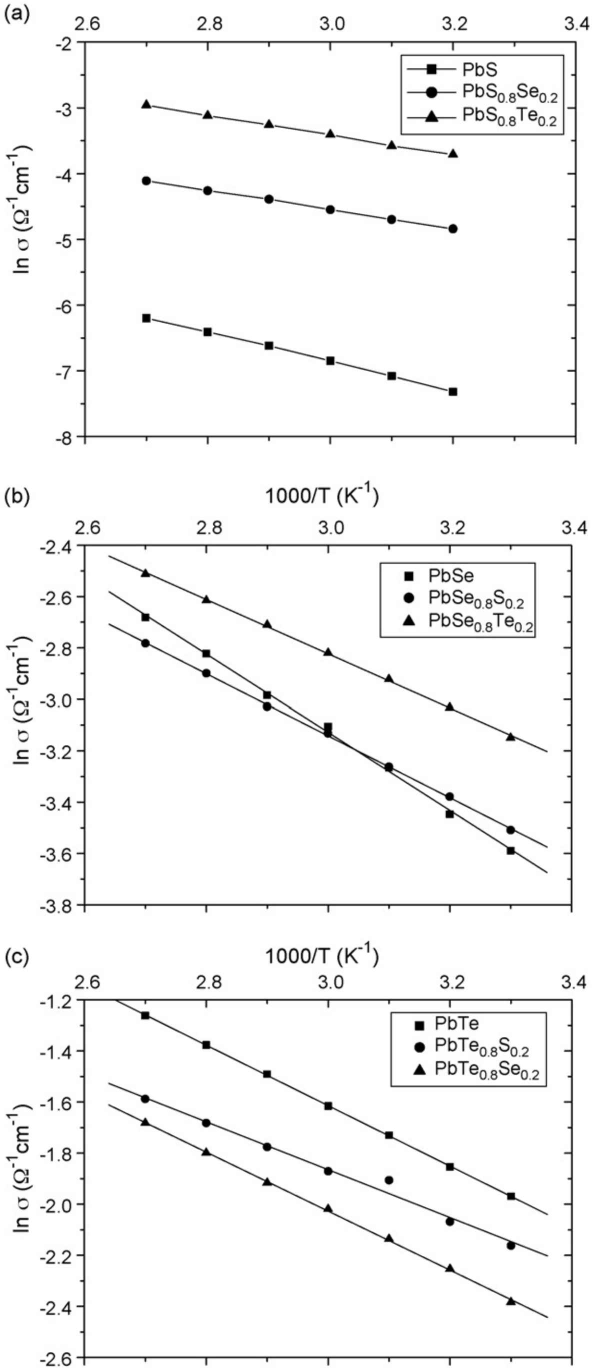

Fig. 2. (a) ln σ versus 1000/T plot for PbS, $PbS_{0.8}Se_{0.2}$ and $PbS_{0.8}Te_{0.2}$. (b) ln σ versus 1000/T plot for PbSe, $PbSe_{0.8}S_{0.2}$ and $PbSe_{0.8}Te_{0.2}$. (c) ln σ versus 1000/T plot for PbTe, $PbTe_{0.8}S_{0.2}$ and $PbTe_{0.8}Se_{0.2}$.

the materials. The dc electrical conductivity of a semiconductor at temperature T is given by

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \tag{3}$$

where ΔE is the activation energy for the generation process and k is the Boltzmann constant. We may write

$$\ln \sigma_{dc} = -\left(\frac{\Delta E}{1000k}\right)\left(\frac{1000}{T}\right) + \ln \sigma_0 \tag{4}$$

When we plot a graph between $\ln \sigma_{dc}$ and 1000/T, a straight line is obtained having slope ($\Delta E/1000k$) and intercept $\ln \sigma_0$.

Thin films of undoped and doped lead salts were studied for their dc conductivity (σ_{dc}) and activation energy (ΔE) in temperature range 300–380 K. Fig. 2(a–c) shows the temperature dependence of dark conductivity for thin films. The conductivity of all these samples increases with increase in temperature showing the semiconducting behaviour of these samples. Lead chalcogenides and their solid solutions have electrically active native point defects (vacancies and interstitials atoms) which produce energy states lying either above the bottom of the conduction band (donor defects) or below the top of the valence band (acceptor defects). This leads to a high charge carrier concentration in undoped crystals because of the deviation of composition from stoichiometry [20]. The plots of $\ln \sigma_{dc}$ against 1000/T are straight lines for all the samples indicating that conduction in these samples is through thermally activated process. The results of other workers [29,30] on the polycrystalline films of lead chalcogenides support the thermally activated conduction. The activation energy for these samples has been calculated by using the slope of curve plotted between $\ln \sigma_{dc}$ and 1000/T. The values of dc conductivity and activation energy of these samples are given in Table 1.

3.3. *Structural characterization*

X-ray diffraction patterns give valuable information about the structure of samples. X-ray diffraction traces of all samples were taken at room temperature and found to show almost similar trends as shown in Fig. 3(a–c). The presence of sharp structural peaks in these XRD traces confirmed the polycrystalline nature of samples. The plane spacing values (d) are experimentally determined from Bragg's relation $2d_{hkl} \sin\theta = n\lambda$ (in our case $n = 1$, $\lambda = 1.5405$ Å) by taking θ-values from the peaks of XRD patterns.

Vegard's law states that the value of lattice parameters of an alloy, as obtained by X-ray data, is the linear function of concentrations of constituent crystals and is expressed as [31]:

$$r = f_1 r_1 + f_2 r_2 \tag{5}$$

where r_1 and r_2 are the lattice parameters of the constituent crystals and r that of the alloy. f_1 and f_2 are the mole fractions of the constituent crystals. The d-values are in good agreement with the ASTM data or data obtained from Vegard's law for doped lead salts films confirming the rock salt (NaCl) structure.

The lattice constants can be determined by combining the Bragg's law and the plane spacing equation for cubic crystal [32]:

$$\sin^2 \theta_{hkl} = \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2) \tag{6}$$

This equation predicts, for a particular incident wavelength λ and a particular cubic crystal of unit cell size a, all the possi-

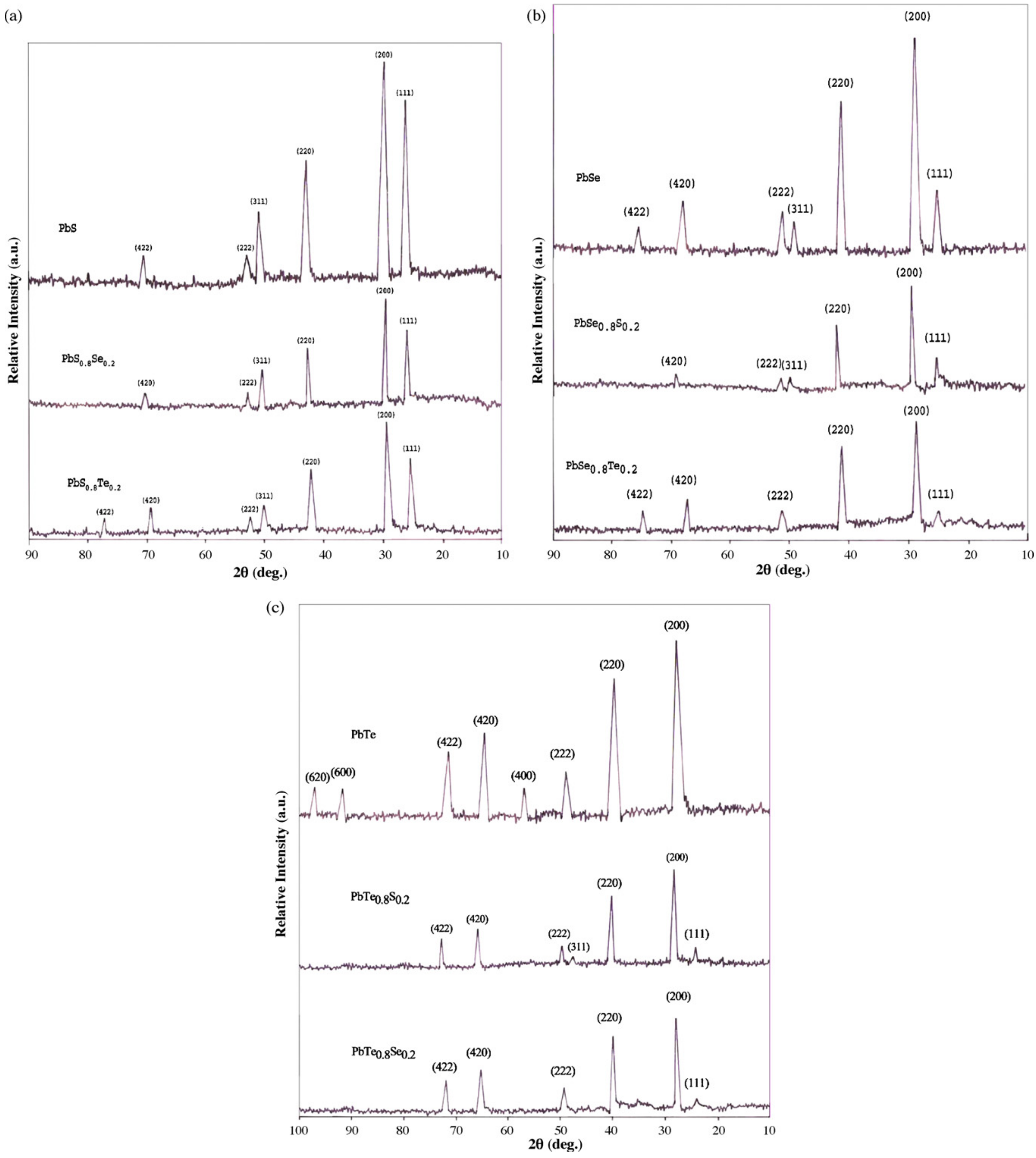

Fig. 3. (a) X-ray diffraction patterns of PbS, $PbS_{0.8}Se_{0.2}$ and $PbS_{0.8}Te_{0.2}$. (b) X-ray diffraction patterns of PbSe, $PbSe_{0.8}S_{0.2}$ and $PbSe_{0.8}Te_{0.2}$. (c) X-ray diffraction patterns of PbTe, $PbTe_{0.8}S_{0.2}$ and $PbTe_{0.8}Se_{0.2}$.

ble Bragg angles at which diffraction can occur from the planes ($h\,k\,l$).

For each undoped and doped lead salts film, the peak intensity of X-ray diffracted beam is obtained for (2 0 0) plane. The lattice constant (a) and plane spacing (d) calculated for each sample are shown in Table 1. The lattice parameters of each ternary system of doped lead salts follow the Vegard's law meaning that within the experimental errors, the lattice parameter of these ternary systems can be linearly interpolated from the lattice constants of the corresponding lead salts.

4. Conclusions

In view of the fact that pseudo-binaries of lead chalcogenides form well miscible solid solutions over a wide composition range, the recent trend in this field is the synthesis and characterization of polycrystalline ternary systems. The variation of band gap through compositional change has enabled the fabrication of detectors and tunable emitters of coherent radiations. The electrical conduction process in the films is through thermally activated process. All the synthesized films were found to be polycrystalline in nature as confirmed by XRD patterns and have a predominantly rock salt (NaCl) structure.

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