Investigations on the properties of solid solutions of pseudo-binary lead chalcogenides

Sushil Kumar [a,*], Bhajan Lal [a], Sunil Rohilla [b], P. Aghamkar [a], M. Husain [c]

[a] Department of Physics, Chaudhary Devi Lal University, Sirsa-125055, Haryana, India
[b] Department of Physics, Guru Jhambheshwer University of Science & Technology, Hisar-125001, Haryana, India
[c] Department of Physics, Jamia Millia Islamia (Central University), New Delhi-110025, India

ARTICLE INFO

ABSTRACT

Lead chalcogenides and their solid solutions with detecting and lasing capabilities have great technological importance. High quality polycrystalline thin films of solid solutions of pseudo-binary lead chalcogenides have been deposited onto ultra clean glass substrates by vacuum evaporation technique. Optical, electrical and structural properties of the thin films of the solid solutions of pseudo-binary lead chalcogenides have been investigated. Absorption coefficient and band gap of films were determined by absorbance measurements in wavelength range 2500–5000 nm using FTIR spectrophotometer. dc conductivity and activation energy of films were measured in temperature range 300–380 K using two probe I–V characteristics method. Crystal structure and lattice parameters of films were determined from X-ray diffractogram.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

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

Narrow band gap and high carrier mobilities identify lead chalcogenides as basic materials for infrared opto-electronic devices [2] and thermoelectric materials in two dimensions 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, photoresisters, lasers, solar cells, opto-electronic 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 solid solutions 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].

Solid solution is one of the main tools for tuning free carrier concentration in semiconductors. Several researchers reported that the solid solutions of IV–VI semiconductors with variable amount of elements results in the appearance of a range of unusual effects that were not characterizing the pure materials [16–18]. The effect of composition of solid solutions on the optical, electrical and

* Corresponding author. Tel.: +91 1666 239835.
  E-mail addresses: sushil.phys@gmail.com, vishu4up1181@gmail.com (S. Kumar).

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

This communication is in continuation of previous research work of the authors [24] in which authors prepared and characterized the samples $PbS_{1-x}Se_x$ and $PbSe_{1-x}Te_x$ and $PbTe_{1-x}S_x$ with composition $x = 0.2$ and 0.8. In order to study the complete series ($x = 0.0$–1.0), in the present work authors synthesized the pseudo-binary solid solutions of lead chalcogenides of $PbS_{1-x}Se_x$ and $PbSe_{1-x}Te_x$ and $PbTe_{1-x}S_x$ with composition $x = 0.4$ and 0.6; and investigates the optical, electrical and structural properties of thin films of these solid solutions.

2. Experimental details

Melt-quenching technique has been employed to prepare polycrystalline bulk solid solutions of pseudo-binary lead chalcogenides. 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 $900\,^\circ$C at a rate of $5\,^\circ$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 thin films were annealed in the same vacuum chamber at about $100\,^\circ$C for 2 h and remain inside the vacuum chamber for 24 h to attain thermodynamic equilibrium as suggested by Abkowitz [25]. Thickness of thin films has been measured using quartz crystal thickness monitor. Deposition parameters were kept same for all thin films.

Absorbance spectra of thin films of solid solutions of pseudo-binary lead chalcogenides were measured in wavelength range 2500–5000 nm using Fourier transform infrared spectrophotometer (Nicolet, Impact, model 410). For electrical conductivity, narrow thin 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 by two probe method. For low field measurements, a dc voltage source in the form of a dry cell of 1.5 V has been used. Temperature of thin films was measured by a copper-constantan thermocouple and was increased by a step value of $2.5\,^\circ$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 solid solutions of pseudo-binary lead chalcogenides 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 l_0/l_t, where l_0 is the incident intensity and l_t is the intensity after traversing a thickness t in the sample [26,27].

$$\text{Absorption coefficient} = \frac{\text{optical density}}{\text{thickness}}$$

or

$$\alpha = \frac{1}{t} \log\left(\frac{l_0}{l_t}\right) \qquad (1)$$

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 [28,29]

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

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 chalcogenides the maxima of valence band and the minima of

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

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$_{0.4}$Se$_{0.6}$	0.34	6.05	3.03	0.033	0.12
PbS$_{0.4}$Te$_{0.6}$	0.37	6.24	3.12	0.129	0.19
PbSe	0.29	6.11	3.06	0.051	0.14
PbSe$_{0.4}$S$_{0.6}$	0.37	6.00	3.00	0.027	0.25
PbSe$_{0.4}$Te$_{0.6}$	0.31	6.33	3.17	0.115	0.12
PbTe	0.34	6.47	3.24	0.225	0.11
PbTe$_{0.4}$S$_{0.6}$	0.38	6.13	3.07	0.078	0.23
PbTe$_{0.4}$Se$_{0.6}$	0.30	6.27	3.13	0.081	0.09

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 ($\sim 10^4$ 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 thin films of solid solutions of pseudo-binary lead chalcogenides 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.

3.2. Electrical characterization

Conductivity is an important factor which reveals the important and reliable information about the transport phenomenon of the materials. The dc electrical conductivity of a semiconductor at temperature T is given by

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

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

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

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 solid solutions of pseudo-binary lead chalcogenides 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 [30,31] on the polycrystalline thin films of lead chalcogenides support the thermally activated conduction. The activation energy for these samples have 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.
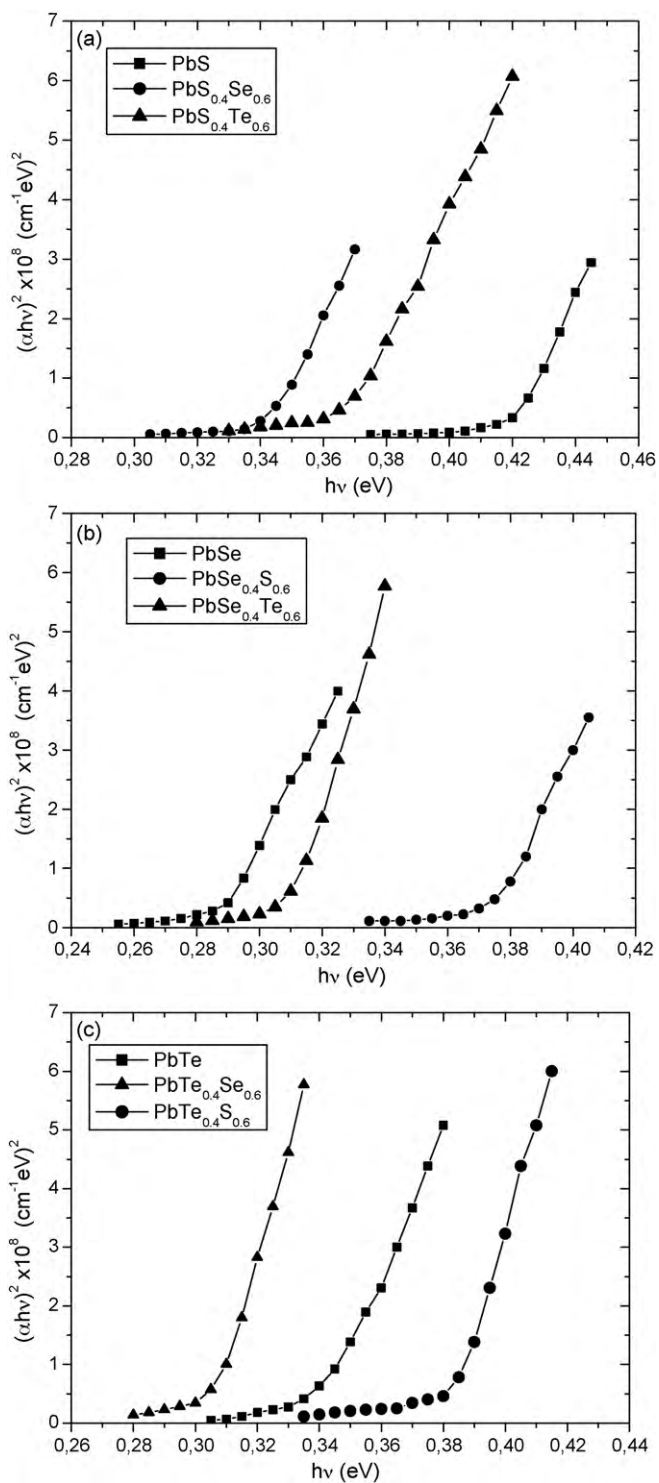
Fig. 1. (a) $(\alpha h\nu)^2$ versus $h\nu$ plot for PbS, $PbS_{0.4}Se_{0.6}$ and $PbS_{0.4}Te_{0.6}$. (b): $(\alpha h\nu)^2$ versus $h\nu$ plot for PbSe, $PbSe_{0.4}S_{0.6}$ and $PbSe_{0.4}Te_{0.6}$. (c): $(\alpha h\nu)^2$ versus $h\nu$ plot for PbTe, $PbTe_{0.4}S_{0.6}$ and $PbTe_{0.4}Se_{0.6}$.

Fig. 2. (a) $\mathrm{Ln}\,\sigma$ versus $1000/T$ plot for PbS, $PbS_{0.4}Se_{0.6}$ and $PbS_{0.4}Te_{0.6}$. (b) $\mathrm{Ln}\,\sigma$ versus $1000/T$ plot for PbSe, $PbSe_{0.4}S_{0.6}$ and $PbSe_{0.4}Te_{0.6}$. (c) $\mathrm{Ln}\,\sigma$ versus $1000/T$ plot for PbTe, $PbTe_{0.4}S_{0.6}$ and $PbTe_{0.4}Se_{0.6}$.

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
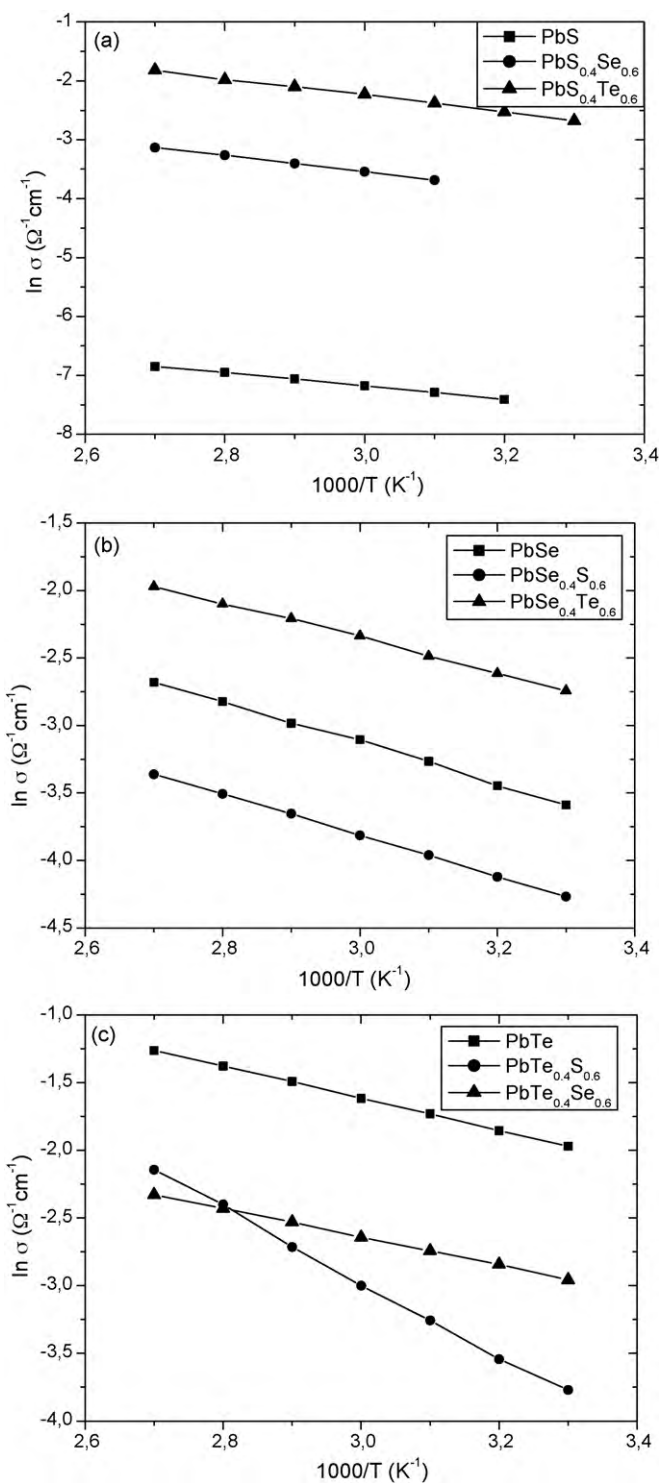
Bragg's relation $2d_{hkl}\sin\theta = n\lambda$ (in our case $n = 1$, $\lambda = 1.5405\,\text{Å}$) by taking θ-values from the peaks of XRD patterns.

Vegard's law states that the value of lattice parameters of an alloy, as obtained by X-ray data, are the linear function of concentrations of constituent crystals and are expressed as [32]
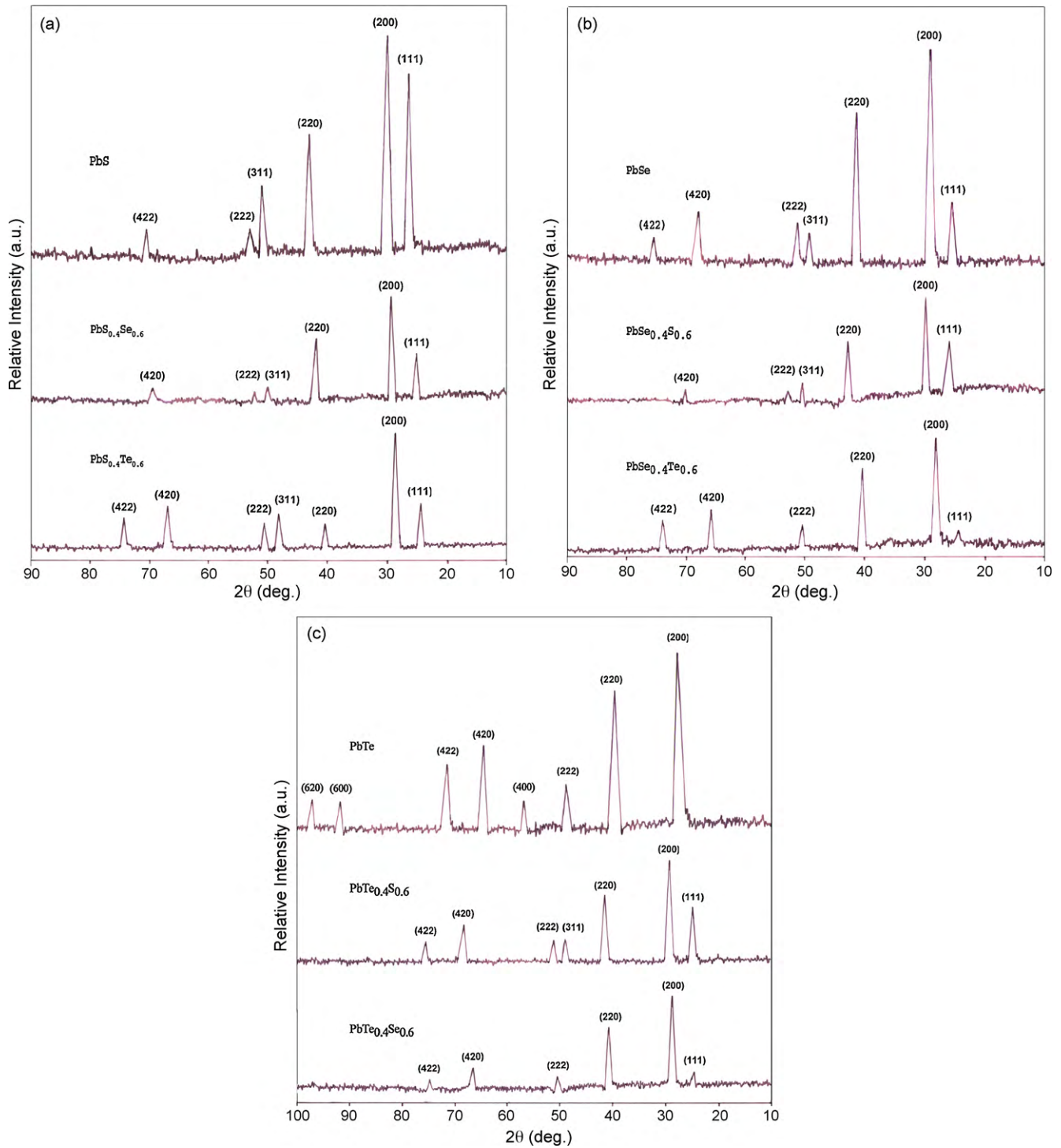
$$r = f_1 r_1 + f_2 r_2 \tag{5}$$

Fig. 3. (a) X-ray diffraction patterns of PbS, PbS$_{0.4}$Se$_{0.6}$ and PbS$_{0.4}$Te$_{0.6}$. (b) X-ray diffraction patterns of PbSe, PbSe$_{0.4}$S$_{0.6}$ and PbSe$_{0.4}$Te$_{0.6}$. (c) X-ray diffraction patterns of PbTe, PbTe$_{0.4}$S$_{0.6}$ and PbTe$_{0.4}$Se$_{0.6}$.

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 [33]

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

This equation predicts, for a particular incident wavelength λ and a particular cubic crystal of unit cell size a, all the possible Bragg angles at which diffraction can occur from the planes ($h\,k\,l$).

For each thin film of solid solutions of pseudo-binary lead chalcogenides, 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 is shown in Table 1. The lattice parameters of each solid solution of pseudo-binary lead chalcogenides follow the Vegard's law meaning that within the experimental errors, the lattice parameter of these solid solutions

can be linearly interpolated from the lattice constants of the corresponding lead chalcogenides.

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 has been the preparation 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 films were found to be polycrystalline in nature as confirmed by XRD patterns and have a predominantly rock salt (NaCl) structure.

References

[1] D. Khokhlov (Ed.), Lead Chalcogenides: Physics & Applications, Taylor & Francis, New York, 2003.
[2] A.M. Samoylov, M.K. Sharov, S.A. Buchnev, A.M. Khoviev, E.A. Dolgopolova, J. Cryst. Growth 240 (2002) 340.
[3] M.S. Dresselhaus, G. Dresselhaus, X. Sun, Z. Zhang, S. Cronin, T. Koda, J.Y. Ying, Microsc. Therm. Eng. 3 (1999) 89.
[4] H. Zogg, M. Arnold, Infrared Phys. Technol. 49 (2007) 183.
[5] I.N. Chao, P.J. McCann, W.L. Yuan, E.A. Orear, S. Yuan, Thin Solid Films 323 (1998) 126.
[6] F.J. Meca, M.M. Quintas, F.J.R. Sanchez, Sens. Actuators 84 (2000) 45.
[7] Z. Dashevsky, S. Shusterman, M.P. Dariel, J. Appl. Phys. 92 (2002) 1425.
[8] I. Pop, C. Nascu, V. Ionescu, E. Indrea, I. Bratu, Thin Solid Films 307 (1997) 240.
[9] S. Chatterjee, U. Pal, Opt. Eng. 32 (1993) 2923.
[10] Q. Li, Y. Ding, M. Shao, J. Wu, G. Yu, Y. Qian, Mater. Res. Bull. 38 (2003) 539.
[11] T. Story, Acta Phys. Polym. A 92 (1997) 663.
[12] G. Nimtz, B. Schlicht, R. Dornhaus, Narrow Gap Semiconductors, Springer, Berlin, 1993.
[13] J.N. Zemel, in: C.G. Scott, C.E. Reed (Eds.), Surface Physics of Phosphors and Semiconductors, Academic Press, London, 1975, pp. 523–562.
[14] A. Lambrecht, R. Kurbel, M. Agne, Mater. Sci. Eng. 21 (1993) 217.
[15] M. Agne, A. Lambrecht, U. Schiessl, M. Tacke, Infrared Phys. Technol. 35 (1994) 47.
[16] T. Story, Acta Phys. Polym. A 94 (1998) 189.
[17] I.I. Vanckik, D.R. Khokhlov, A.V. Morozov, A.A. Tarekhov, E.I. Slynko, V.I. Sylnko, A. deVisser, W.D. Dobrowlski, Phys. Rev. B61 (2001) 889.
[18] M.M. Ibrahim, E.M.M. Ibrahim, S.A. Saleh, A.M. Abdel Hakeem, J. Alloys Compd. 429 (2006) 19.
[19] M.M. Ibrahim, S.A. Saleh, E.M.M. Ibrahim, A.M. Abdel Hakeem, J. Alloys Compd. 452 (2008) 200.
[20] J. Trajic, A. Golubovic, M. Romcevic, N. Romcevic, S. Nicolic, V. Nikiforov, J. Serb. Chem. Soc. 72 (2007) 55.
[21] P.P. Hankare, S.D. Delekar, P.A. Chate, S.D. Sabane, K.M. Daradkar, V.M. Bhuse, Semicond. Sci. Technol. 20 (2005) 257.
[22] V.N. Vodopyanov, M.M. Kondratenko, Russ. Phys. J. 39 (1996) 649.
[23] R.R. Dalouche, S. Rolland, R. Granger, C.M. Pelletier, Phys. Status Solidi (b) 129 (2006) 835.
[24] S. Kumar, B. Lal, P. Aghamkar, M. Husain, J. Alloys Compd. 488 (2009) 334.
[25] M. Abkowitz, Polym. Eng. Sci. 24 (1984) 1149.
[26] K.A. Rubin, M. Chen, Thin Solid Films 181 (1989) 129.
[27] D.P. Gosain, I. Shimizu, M. Ohmura, M. Suzuki, T. Bando, S. Okano, J. Mater. Sci. 26 (1991) 3271.
[28] Y.I. Ravich, B.A. Effimova, I.A. Smirnov, Semiconducting Lead Chalcogenides, Plenum Press, New York, 1970.
[29] J.I. Pankove, 'Optical Processes in Semiconductors', Prentice-Hall Inc., New Jersey, 1971.
[30] S. Espevick, Chen-ho Wu, R.H. Bube, J. Appl. Phys. 42 (1971) 3513.
[31] F. Briones, D. Galmayo, C. Ortiz, Thin Solid Films 78 (1981) 385.
[32] R.F. Bis, J.R. Dixon, J. Appl. Phys. 40 (1969) 1918.
[33] B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley Publishing Co. Inc., Massachusetts/London, 1959.