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# Properties of X-ray diffraction and Raman scattering in PbSe, PbS and $PbS_{0,5}Se_{0,5}$ thin films

S.N. Yasinova[a,*], S.I. Mekhtiyeva[b],M.H.Huseynaliyev[a],R.I. Alekberov[b]
[a]*The Ministry of Science and Education of Azerbaijan, Institute of NaturalResources, H.Aliyev ave. 76, AZ7000, Nakhchivan,Baku, Azerbaijan*
[b]*The Ministry of Science and Education of Azerbaijan, Institute of Physics named after Academician Hasan Abdullayev,G. Javid ave 131, AZ1143. Baku, Azerbaijan*

Structural properties of PbSe, PbS and $PbS_{0.5}Se_{0.5}$ thin films and mechanisms of combinational scattering of light from phonons were studied by X-ray diffraction and Raman spectroscopy methods. The results of X-ray diffraction show that the crystallite sizes found in the thin layers of the studied substances are in the order of nanometers and vary in the interval d~10.7 ÷ 30.8 nm. It was determined that the scattering bands of the $PbSe_{0.5}S_{0.5}$ sample with large nanoparticle sizes shift to the region of large wave numbers compared to the scattering bands observed in the region of low wave numbers.

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## 1. Introduction

In recent years, scientific research devoted to the optical properties of narrow-bandgap semiconductors with colloidal quantum dots has been growing intensively. One of the main reasons for this is that group IV-VI narrow-bandgap semiconductors have a two-photon absorption feature in the near and mid-infrared region of the spectrum. Another reason is its successful application in optical devices with low financial cost[1]. From the conducted studies, it is concluded that it is possible to adjust the optoelectronic properties of lead chalcogenides (PbSe and PbS) by the following methods: thermal treatment, changing the relative concentration of the chalcogen components included in the composition, changing the diametrical dimensions of the controllable quantum dots (in the range of 8.1÷16.1 nm) as a result of the joint effect of the mentioned [2]. Other studies show that the control of nanoparticle sizes in the intervals of 1.32 ÷ 2.26 nm and 1.28–2.48 nm in PbS(PbSe) materials obtained by the hot injection method, depending on the technological mode, lays the background for purposeful control of structural, optical and electrical properties [3].

Thus, the comparative analysis of the articles devoted to the structure and optoelectronic properties of lead chalcogenides (PbSe and PbS) shows that in order to obtain properties with the required physical characteristics in the studied substances, it is of great importance to implement the appropriate synthesis technology, technological regime and conditions, and composition modification. On the other hand, the selection of technological methods with high efficiency is one of the important conditions for the successful implementation of the mentioned works. From this point of view, among the known methods of obtaining a PbS thin film, the one that attracts more attention due to its simplicity and effectiveness is the chemical bath deposition technology from solution using thiamides as chalcogenizer, primarily thiourea [4]. From the comparative analysis of the studies, we conclude that in the presented article it will be possible to purposefully control the following by applying the chemical bath deposition method to obtain thin layers of lead chalcogenides (PbSe and PbS): By changing the pH, temperature and concentration of the solution, the nano-size of the crystallites, the thickness of the thin layers, the quality, the deposition rate and due to them, the structure and Raman scattering properties of the obtained substances [5].

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[*] Corresponding author: sara.novruzova@yahoo.com

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The purpose of the article is to analyze the changes in the structural properties of lead chalcogenides (PbSe and PbS) thin films obtained by chemical bath deposition and the mechanisms of their influence on Raman scattering.

## 2. Experimental details

The solution used for obtaining the PbS thin film by chemical bath deposition is prepared by taking equal amounts (by volume) of each of the solutions prepared in the following manner: lead acetate $Pb(CH_3COO)_2$ - 0.07 M; sodium hydroxide (NaOH)-0.3 M; triethanolamine $N(CH_2CH_2OH)_3$-0.06 M; thiourea $(NH_2)_2CS$-0.17 M. The chemical bath deposition process was carried out at 40°C in a 60 ml beaker. A glass base is placed inside the solution in a vertical position beforehand, and the solution is constantly stirred with a magnetic stirrer during the entire process. After 20 minutes, the glass substrate is removed from the solution and washed in distilled water and dried.

The solution usedfor obtaining a thin layer of PbSe by chemical bath deposition at a temperature of 60°C is preparedby taking the same amount (by volume) from each of the solutions prepared in the following manner: lead acetate $Pb(CH_3COO)_2$ - 0.07 M; sodium hydroxide (NaOH)-0.3 M; triethanolamine $N(CH_2CH_2OH)_3$-0.06 M; sodium selenosulfate $Na_2SSeO_3$-0.17 M.The sodium selenosulfate solution used to enter the selenium component into the solution was obtained by boiling 0.425 g of metallic selenium powder and 1.245 g of sodium sulfide in 100 ml of distilled water at a temperature of 90°C in arefrigerator for 7 hours [6].The chemical bath deposition process was carried out in a 60-milliliter laboratory beaker at a temperature of 60°C. A glass base is placed inside the solution in a vertical position beforehand, and the solution is constantly stirred with a magnetic stirrer during the whole process. After 20 minutes, the glass substrate is removed from the solution and washed in distilled water and dried. After this process, a homogeneous PbSe thin layer with good adhesion was obtained on the glass substrate and on the walls of the used laboratory beaker. In the process of obtaining thin layers, the PbSe finepowder separated from the solution in the form of sediment as the main mass was studied separately after washing with distilled water and drying. PbSe thin film and finepowderwere obtained simultaneously at room temperature.Lead acetate $Pb(CH_3COO)_2$ - 0.07 M; sodium hydroxide (NaOH)-0.3 M; triethanolamine $N(CH_2CH_2OH)_3$-0.06 M; sodium selenosulfate $Na_2SSeO_3$-0.17 M are obtained by adding an equal amount (12 mL) of each solution to a 60-milliliter laboratory beaker, placing the test tube vertically.After mixing with a magnetic stirrer for 40 minutes at room temperature, we keep it undisturbed for 1 day (24 hours). As a result, a thin layer of PbSe with good adhesion is obtained both on the test glass and on the wall of the laboratory beaker. PbSe fine powder is obtained as asediment at the bottom of the solution. Research works are carried out after the sediment is washed and cleaned with distilled water.

Applying the methods of obtaining PbS and PbSe thin films, we obtained $PbS_{0.5}Se_{0.5}$ thin film in solid solution. The components needed to obtain a thin layer of $PbS_{0.5}Se_{0.5}$ by chemical bath deposition at room temperature are: lead acetate $Pb(CH_3COO)_2$ - 0.07 M; sodium hydroxide (NaOH)-0.3 M; triethanolamine $N(CH_2CH_2OH)_3$-0.06 M; sodium selenosulfate $Na_2SSeO_3$-0.17 M; thiourea $(NH_2)_2CS$-0.17 M. The reaction is carried out by adding equal amounts (12 ml) of each component of lead acetate, sodium hydroxide and triethanol, and adding sodium selenosulfate and thiourea in a ratio of 50:50, that is 6 ml of each. The test tube is placed vertically in a 60 milliliter laboratory beaker. After mixing with a magnetic stirrer for 40 minutes at room temperature, it is stored undisturbed for 1 day (24 hours). The glass substrate is removed from the solution and washed with distilled water. After drying, we see the formation of a $PbS_{0.5}Se_{0.5}$ thin layer with good adhesion. Considering the weight of the glass before and after the reaction, the thin layer was calculated to be 3.5 nm. Measurement of the X-ray diffraction scattering spectra of the obtained PbS, PbSe and $PbS_{0.5}Se_{0.5}$ thin films was performed with a D-8 ADVANCE diffractometer.

## 3. Results and discussions

Figure 1a (b, c) shows X-ray diffraction curves of PbSe, PbS and $PbS_{0.5}Se_{0.5}$ thin films.The crystallite sizes of nanoparticles belonging to PbSe, PbS and $PbS_{0,5}Se_{0,5}$ were calculated by applying the Debye-Scherrer formula given below to the results obtained in Figure 1. The obtained results are described in Table 1.

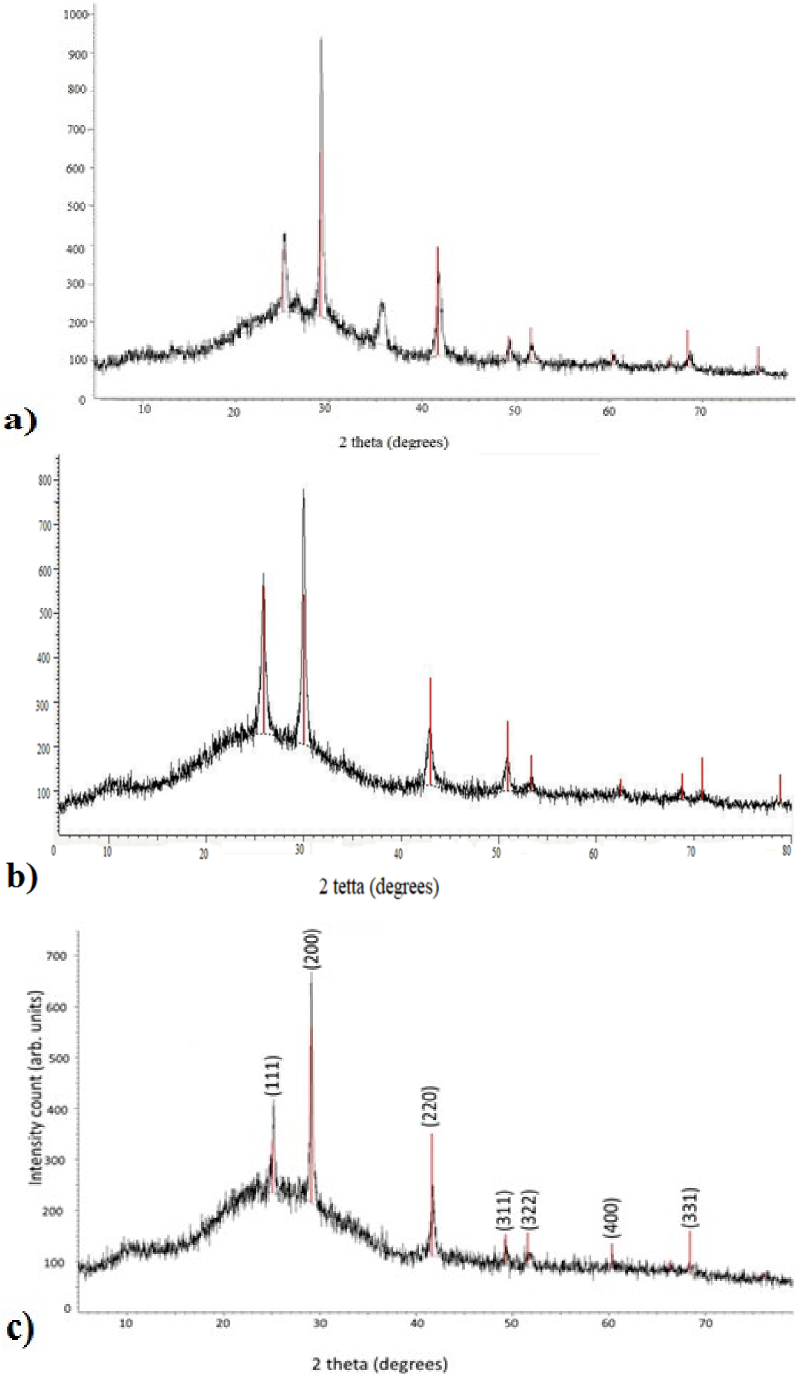

*Fig. 1. X-ray diffraction curves of PbSe (a), PbS (b) and $PbS_{0.5}Se_{0.5}$ (c) thin films.*

In formula (1), **d** is the crystallite size of nanoparticles, **λ** is the wavelength of the X-ray beam ($\lambda$=1.54 Å), β is the half-width of the sharp maxima described in the X-ray diffraction scattering curves of the samples, and **θ** is the Bragg reflection angle.

$$d = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

We should note that the values of scattering angle (2θ) shown in Table 1 correspond to diffraction scattering from planes with Miller indices (111), (200), (220), (311), (322).

*Table 1.The scattering angle (2θ), the crystallite size (d) of nanoparticles, the half-width (β) of the sharp maxima.*

| **Parameters** | **PbS** | **PbSe** | **$PbSe_{0.5}S_{0.5}$** |
|---|---|---|---|
| $2\theta_1$ | 25,91° | 25.24° | 25.22° |
| $\beta_1$ | 0,67 | o.55 | 0.44 |
| $d_1$ | 12,1 nm | 14.8 nm | 18 nm |
| $2\theta_2$ | 29,98° | 29.31° | 29.15° |
| $\beta_2$ | 0,7 | 0.77 | 0.46 |
| $d_2$ | 11,7 nm | 10.7 nm | 17.9 nm |
| $2\theta_3$ | 42,98° | 35.65° | 41.65° |
| $\beta_3$ | 0,61 | 0.72 | 0.45 |
| $d_3$ | 14,1 nm | 11.6 nm | 30.8 nm |

As can be seen from Table 1, the crystallite sizes found in the thin layers of PbSe, PbS and $PbS_{0,5}Se_{0,5}$ compounds are in the order of nanometers and vary in the range of 10.7 ÷ 30.8 nm. On the other hand, it is known from the obtained results that the crystallite sizes of nanoparticles change significantly when the studied substances are subjected to compositional modification. It was determined that the replacement of sulfur (S) with selenium (Se) (in full proportion) increases the crystallite size, which is calculated mainly according to the values of the scattering angle (2θ). However, the replacement of sulfur (S) with selenium (Se) in half ratio increases the crystallite size calculated for all values of the scattering angle (2θ) ($2\theta_1$, $2\theta_2$, $2\theta_3$ ) (Table 1). In order to compare the obtained results, Raman scattering spectra of thin layers of PbSe, PbS and $PbS_{0.5}Se_{0.5}$ compounds were measured and depicted in Figure 2.Studies show that the Raman spectroscopy method, as in various semiconductor materials, is one of the effective methods for identifying the structure of lead chalcogenides (PbSe, PbTe, PbS) [7]. It should be noted that Raman scattering allows determining the dynamics of oscillations associated with optical and acoustic phonons, rotation and other low-frequency oscillation modes in crystalline, amorphous, polymer, liquid, proteins, etc. materials. Physically, it is based on the inelastic scattering of monochromatic light from virtual vibrational states of matter or molecular vibrations. Given that the materials obtained from the diffraction scattering curves depicted in Figure 1 have a crystalline structure, it was expected that three different modes of phonons (1. longitudinal optical phonons, 2. transverse optical phonons 3. surface phonons) would be observed in the Raman scattering spectrum depicted in Figure 2, analogous to semiconductors with a crystalline structure.However, studies show that transverse and surface phonon modes are usually not observed due to symmetry constraints [7]. Also, since the samples studied in the article do not have a high-quality crystal structure, the 1st order Raman effect is not observed. The research conducted in this direction reveals the presence of considerable uncertainty and necessitates conducting new research. The main reason for the mentioned uncertainty is the observation of rapid photooxidation processes in thin layers of PbS and PbSe under the influence of laser radiation applied to observe Raman scattering [8]. In particular, while weak Raman scattering is expected to be observed in the region of relatively low wave numbers (154, 205 and 454 $cm^{-1}$) in PbS, photooxidation processes occurring on the surface of thin films under the influence of a laser beam artificially enhance the Raman scattering signal [8]. Other similar articles also show that the peaks observed at relatively low frequencies (94.6; 113; 132.7 and 275 $cm^{-1}$) of the Raman spectrum belonging to thin films of Pb-Se systems are mainly related to lead oxide compounds [9]. The above makes it difficult to observe the pure Raman scattering characteristic of matter.In this regard, studies show that the peak observed in the Raman scattering spectrum of PbS at the value of 135 $cm^{-1}$ is mainly due to Pb-O-Pb strain bonds[8].Taking into account that the peaks at the values of 148, 115 and 136 cm$^{-1}$ of the wave number were observed in the Raman scattering spectra of thin layers of PbSe and $PbS_{0.5}Se_{0.5}$compounds in the presented article, it can be concluded that the obtained results partially agree with the results of works [8-9].Based on the results of X-ray diffraction scattering in Table 1, if we consider that the calculated crystallite sizes of nanoparticles of the studied substances take different values depending on the compositional modification, it is understandable that the peaks related to Pb-O-Pb strain bonds are observed at different wave numbers (148, 115 and136 cm$^{-1}$). Those results show that peaks belonging to Pb-O-Pb strain bonds formed due to oxidation processes are more intensively observed in $PbS_{0,5}Se_{0,5}$ with relatively large calculated crystallite sizes of nanoparticles.The observation of those peaks at relatively close and different wave numbers is due to the fact that the crystallite sizes of nanoparticles have different values (Table 1). In a number of studies, it is noted that the scattering peak observed at 138 cm$^{-1}$ is related to longitudinal optical phonon modes [7].

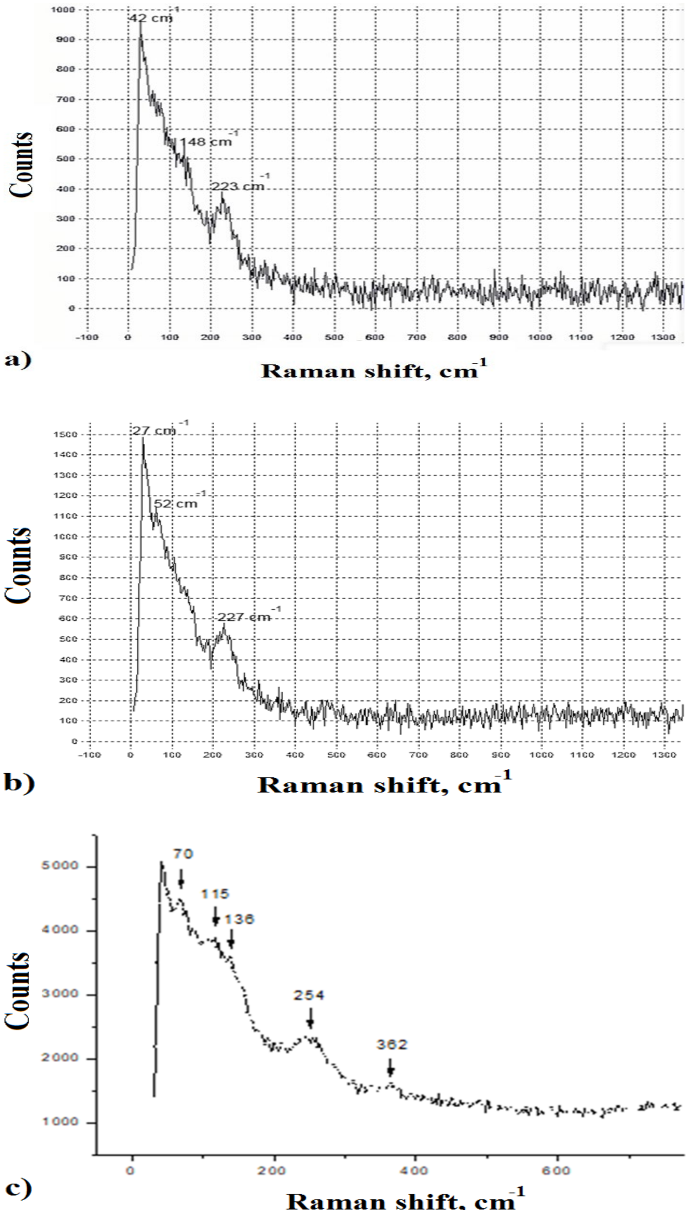

*Fig. 2. Raman spectra of PbSe(a), PbS(b) and $PbS_{0.5}Se_{0.5}$ (c) thin films obtained by chemical bath deposition.*

In Figure 2, different maxima are observed in the range of wave numbers 50<ν<180 $cm^{-1}$ for all compositions.Despite the fact that the broad set of maxima observed in the range of 50-175 $cm^{-1}$ wavenumbers of the spectrum is generally associated with overtone or phonon modes [10], it is important to investigate them depending on the crystallite size of nanoparticles. The results of tensor calculations on X-ray diffraction and Raman scattering show that longitudinal and transverse optical phonons in the (111) plane of PbSe crystals are Raman active. Therefore, the peaks observed at 135 $cm^{-1}$ and 47.6 $cm^{-1}$ wave numbers of the Raman scattering spectrum of PbSe are associated with longitudinal and transverse optical phonons [11]. The results obtained in Fig. 2a and Fig. 2b show that the observed peaks in the range of 42-52 $cm^{-1}$ can be explained by Raman-active transverse optical phonons scattering on the (111) plane. It is believed that as a result of half-substitution of selenium with sulfur, the shift of the peaks noted in the Raman scattering spectrum (when changing to $PbSe_{0.5}S_{0.5}$) towards relatively large wave numbers (towards 70 $cm^{-1}$) is due to the increase in the crystallite size of the nanoparticles, which gives rise to scattering on the (111) plane. Half-substitution of selenium with sulfur enhances the bonding within the nanoparticles due to the chemical activity and high bond energy of the sulfur atoms along with the size of the nanoparticles. As the elastic force constant (k) increases as a result of the increase in bond connectivity, the frequency of the Raman active oscillation modes expressed below, according to the molecular structure model, increases [12].

This results in the shift of the scattering peak associated with transverse optical phonons in $PbSe_{0.5}S_{0.5}$ to relatively large wave numbers (towards 70 $cm^{-1}$).

$$\nu_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad (2)$$

where k is the elastic force constant that binds adjacent atoms or atomic structural elements, and μ is the reduced mass (or the mass of the optical mode).

Note that the shift of the scattering peak associated with transverse optical phonons towards relatively large wave numbers (towards 70 $cm^{-1}$) is also related to the increase in the percentage of sulfur atoms (compared to selenium) within the nanoparticles, that is, to the decrease in the mass (μ) of the optical mode. The observed maximum of Raman scattering spectra at ~254 $cm^{-1}$ is associated with the presence of $Se_8$ rings in the scientific literature [13]. The peaks observed in the 120 $cm^{-1}$÷122 $cm^{-1}$ interval indicate scattering in case of the joint presence of both transverse and longitudinal optical phonons [14]. For PbS thin films obtained by the epitaxy method, scattering due to double transverse optical phonons was observed in the interval of wave number 186 $cm^{-1}$÷197 $cm^{-1}$ [14-15]. In the presented article, in the samples obtained by chemical bath deposition, depending on the size of the nanoparticles, the above-mentioned scattering band is weakly observed and shifts towards the region of relatively long wave numbers (223 $cm^{-1}$÷227$cm^{-1}$ ). Thus, the obtained results show that either the modification of the composition or the size of the nanoparticles have a significant effect on the photooxidation processes occurring on the surface of the obtained thin films and the scattering bands observed in individual regions. It was determined that the number of scattering bands in the **$PbSe_{0.5}S_{0.5}$** sample with high nanoparticle sizes increases, and the scattering bands observed in the region of low wave numbers shift to the region of relatively large wave numbers.

## 4. Conclusion

It was determined that as a result of semi-substitution of selenium with sulfur, along with the increase in the size of the nanoparticles, the bond within the nanoparticles is strengthened due to the chemical activity and high bond energy of the sulfur atoms. As the elastic force constant (k) increases as a result of the increase in bond connectivity, the frequency of the Raman active oscillation modes expressed below, based on the molecular structure model, increases. The results of X-ray diffraction scattering show that the crystallite sizes found in thin layers of **$PbS_{0,5}Se_{0,5}$** are larger and vary in the range of 17.9÷30.8 nm.

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