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STRUCTURAL AND OPTICAL PROPERTIES OF ZINC SELENIDE CRYSTAL MODIFIED BY ION-EXCHANGE METHOD

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The grown ZnSe crystal has been ion exchanged with silver ions. Ion exchange of ZnSe crystal was carried out in muffle oven. The effect of ion exchange by silver on structural properties has been studied by X-ray Diffraction (XRD). The effect of ion exchange by silver on optical properties such as optical band gap has been calculated from the reflectance spectra in Ultraviolet Visible spectrophotometer (UV-VIS).After ion exchange the ratio of compositions of sample was determined by Energy Dispersive X-ray Spectroscopy analysis (EDAX). The morphology of the surface was studied before and after the process by Scanning Electron Microscopy (SEM).

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1. Introduction

One of the interesting directions in material science is modification of surface area [1] or to obtain the complex structures by ion exchange from electrolyte solutions (core-shell type structures in material science). These processes allow that to change the chemical composition and physical-chemical properties of the material. One of the most perspective direction for to carry out the modification of the surface area of the crystals is diffusion [2] and the ion exchange from melts [3]. This method is widely used for the creation of optical waveguide structure based on lithium niobate and glass [4]. Wide band-gap semiconductors have been a promising research topic for optoelectronics applications such as photovoltaics [5]. ZnSe is one of the perspective materials for infrared optics and optoelectronics [6]. At room temperature, the value of band gap zone is between 2.799 and 2.803eV [7] at $\lambda = 587.6$ nm wavelength and the value of refractive index "n" is 2.6244. The refractive index varies depending on the wavelength. According to, the crystal dispersion also changes when the surface is modified. One of the methods for changing of parameters of the surface area is ion exchange. During ion exchange process, the compound of the surface area is varying, which changes the band gap zone, conductivity, refractive index and other parameters of the crystal structure.

For applications as the buffer layer in solar cells, biomedical labels or in thin film transistors (TFTs), the ZnSe films must have tunable optical properties, electrical conductivity and preferably control over both types of conduction: n-type and p-type [8]. Diffusion and ion exchange depend on several parallel processes and are multifactorial. The temperature and the ions in electrolyte solutions (or in melts) and other factors in influenced the speed of ion exchange process. The nature of the solid base fitting can also affect to this process. It is obvious that, if the structure is porous, the diffusion process will be easier (i.e., the diffusion coefficient is relatively great). This occurs usually in porous systems and polymers.

It should be noted, the main role in this process is the process of interface between the electrolyte solution with the solids, the kinetics of the reactions in the interface, the process of transport of ions into solid and from solid. Moreover, it should be noted that from the viewpoint of create the new phase the process should be thermodynamically beneficial. Since the 70s years of the last century, ion exchange process was a new direction in material science, ion exchange was widely used in the obtain of new materials. Along with the diffusion of metals (or ions), the ion exchange process is also used in the preparation of new structures:

- modification of crystals;
-alloying of materials and nanoparticles;

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- new type of materials.

The ion-exchange methods have been widely used for doping semiconductor materials such as CdS [9], ZnO [10] and CdTe[11].

The ion exchange process allows the modification of the surface area of the material and obtains the various type of new material. The process of ion exchange can be carried out in electrolyte solution and melts. In this study, the ion exchange process of ZnSe crystal was carried out in KCl + $AgNO_3$ melt.

2. Experimental part

For carried out of ion exchange were used the mixture of KNO_3 (melting point 334°C) and silver nitrate - $AgNO_3$ (melting point 209.7°C). The initial sample was ZnSe crystal. Potassium nitrate and silver nitrate salts were mixed in a 10: 1 weight ratio and this mixture was placed in porcelain crucible with ZnSe crystal. Then crucible was heated at 350 °C for 5 hours in the muffle oven. Then the sample was cooled to room temperature. After ion exchange, the color of the crystal changes from yellow to dark gray. The surfaces of the samples have been investigated on microscopes before and after the ion exchange. The structure of the samples was studied by X-ray diffractometer. The optical properties of the samples were investigated by SPECORD-250 plus.

3. Results and discussions

The crystalline structures of sample were investigated by XRD. In Fig.1 was shown XRD pattern of pure ZnSe crystal.

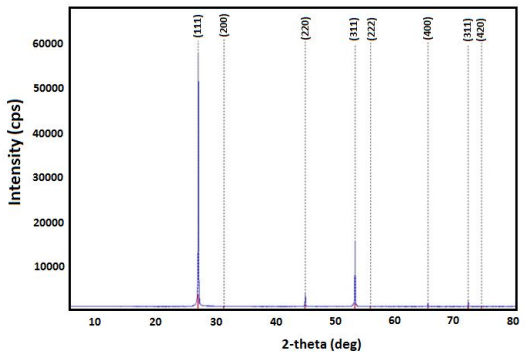


Fig.1. XRD pattern of ZnSe crystal

As seen from the diffraction pattern is observed the angle at the angle 2θ =27°, 32°, 45°, 53°,56°,66°, 72°,75°. It appears compared to literature, ZnSe crystal shows the cubic structure [12]. The peaks can be indexed as (111), (200), (220), (311), (222), (400), (331) and (420), respectively.

The diffraction pattern of ZnSe crsytal after ion exchange in the melt of KNO_3:$AgNO_3$ (10:1) at 350°C is shown in Fig.2.b.The results revealed the orthorhombic structure of Ag_2Se (JCPDS Card No. 24-1041). As can be seen from the picture, the appearance of the diffraction varies considerably after the ion exchange and pure ZnSe crystals were completely transformed to Ag_2Se.

For comparison, surface of modified ZnSe crystal was polished and the diffraction peaks of crystal polishing surface have been shown in Fig.2.a. The polished surface is reveal Ag_2Se. But marked peaks are refer to ZnSe. The ZnSe peaks are increasingly observed on the surface in contrast to the surface area.

It seems from diffraction pattern, the diffraction peaks of the ion exchanged sample are

broad than the initial diffraction peaks. And it is related to the dispersion on the surface area after ion exchange process.

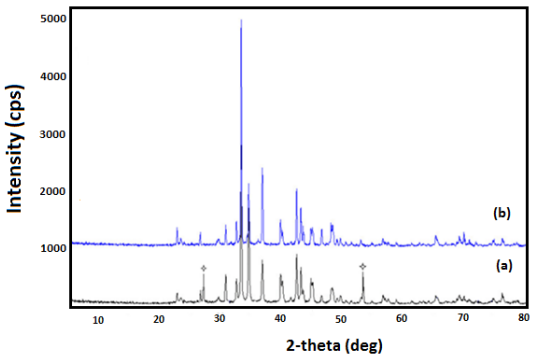
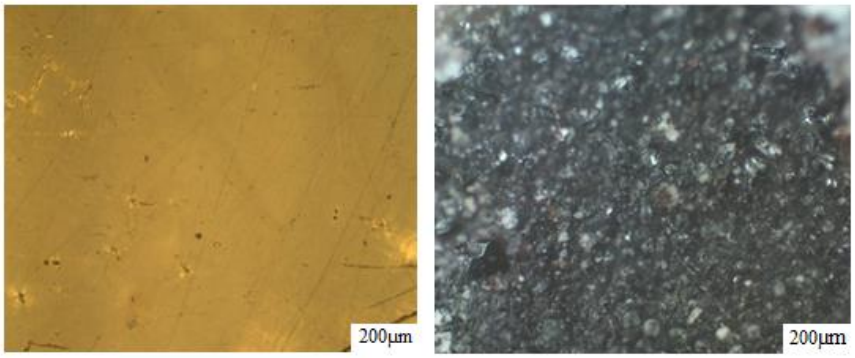


Fig.2. XRD pattern of different layers of ion exchanged ZnSe crystal

It seems from diffraction pattern, the diffraction peaks of the ion exchanged sample are broad than the initial diffraction peaks. And it is related to the dispersion on the surface area after ion exchange process.

3.1. Optical microscopy

Optical microscopy is a very useful technique for examine the appearance of surface of sample. To investigate morphology of samples was used optical microscope. Fig.3 (a) shows the surface images of ZnSe crystal and in Fig. 3 (b) surface images of sample is given after the ion exchange in melt of KNO_3 : $AgNO_3$ (10:1).



a) *b)*

Fig.3.Optical images of crystals.
a) ZnSe crystal; b) after ion exchange of ZnSe crystal

As shown in the Fig.3 (a), the surface of the ZnSe crystal is smooth and (b) the surface area of ZnSe was modified into ZnSe→Ag_2S and becomes to granular after ion exchange.

3.2. Optical studies

The optical properties of samples were investigated by Ultraviolet-Visible (UV-Vis) spectrophotometer. The optical reflectance spectra of ZnSe crystal and ion exchanged ZnSe are recorded in range of 400-900 nm (Fig. 4).

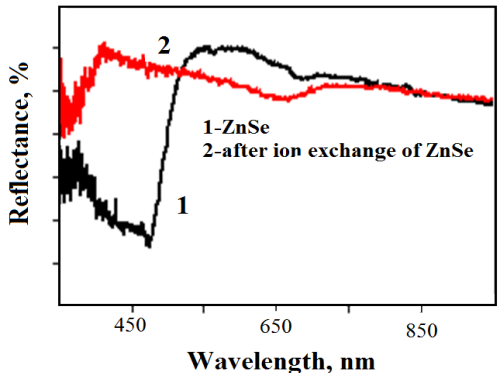


Fig.4. Reflectance spectra of ZnSe and modified ZnSe crystals..

The value of direct band gap of the samples was determined by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. hν graph to the hν axis [13]; as shown in Fig. 5.(a) and (b).

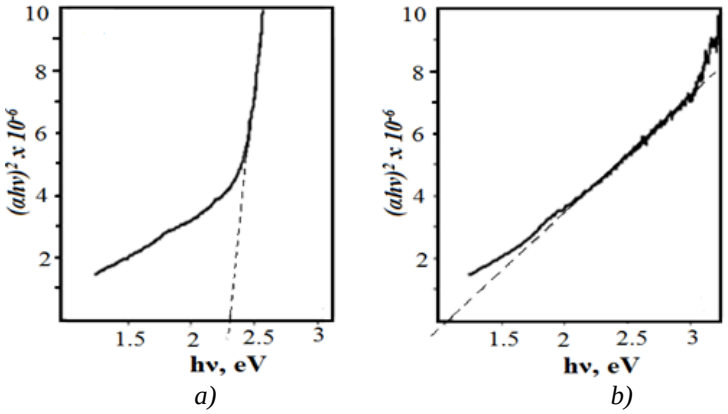
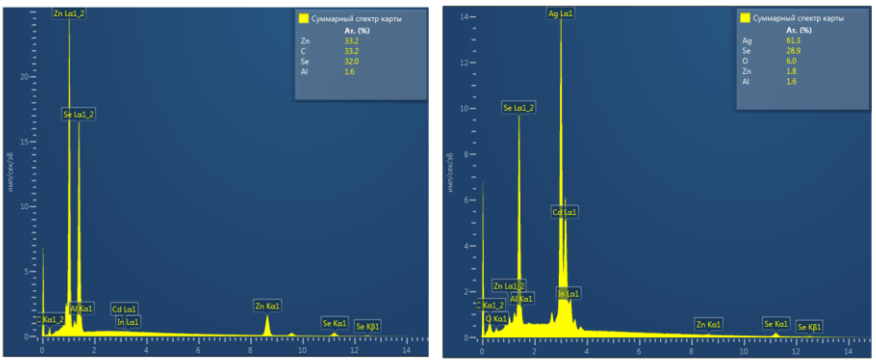


Fig. 5. Determination of band gap of crystal.
a)ZnSe crystal; b) modified ZnSe crystal.

The band gap value of pure ZnSe crystal is 2.3eV. After the ion exchange of ZnSe crystal, the value of band gap decreases to 1.1eV. This is affected the value of band gap due to the removal of zinc atoms from ZnSe crystal by silver atoms in the ion exchange process. This value indicates that, the band gap of sample slide toward band gap zone of Ag_2Se.

3.3. EDAX measurements

EDAX analysis was used for the determination of chemical composition of samples. The EDAX analysis of ZnSe crystal and ion exchanged sample are shown in Fig. 6.



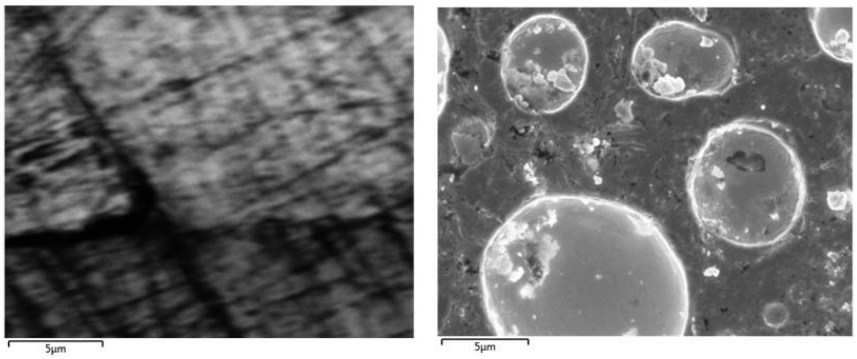
a) *b)*

Fig.6. EDAX measurements of samples.
a) ZnSe; b) modified ZnSe crystal by silver ions.

It is shown that, the results of the initial analysis of the ZnSe sample, atomic ratio of Zn and Se elements are at 33.2 % and 32.0 % respectively, in Fig. 6 (a). Apparently, stoichiometry is as expected. The results of after the ion exchange of ZnSe are shown in Fig.6 (b). After the ion exchange, atomic percentage of Ag and Se are 53.6 and 24.4, respectively. After ion exchange of ZnSe with Ag ions, Zn^{2+} ions were replaced by Ag^{+} ions. As previously mentioned, based on XRD results, Ag_2Se compound was formed. Obviously, during the ion exchange process, Zn^{2+} ions diffuse from crystalline to the alloy and Ag^{+} ions diffuse from the melt to the surface area of crystalline. During this process, they can be interacted with oxygen in the melt and in the air. As a result of this interaction, zinc oxide (ZnO) and silver oxide (Ag_2O) may arise. In the sample, the atomic percentages of O, Zn and Al elements are 13.9%, 5.8% and 1.1%, respectively.

3.4. Morphological studies

The morphological properties of samples were investigated by SEM. The surface of the ZnSe crystal is rough in certain amount is shown in Fig.7 (a). Ionic exchanged ZnSe crystal has created a porous surface on the surface of ZnSe crystal. In addition, particles are formed in the formed pores of the crystal. This is due to, the particles on the surface of the crystal are combined with silver atoms and to form Ag_2Se compound. The formation of both of ZnSe and Ag_2Se compounds on the surface also confirms the results obtained from the XRD and Element analysis.



a) *b)*

Fig.7.SEM images of samples.
a) ZnSe crystal; b) after ion exchange of ZnSe crystal.

4. Conclusions

In summary, the surface modification of ZnSe crystal was carried out by silver ions. After ion exchange of crystal, on the surface area was formed Ag_2Se compound from XRD results. As seen from SEM image, the surface area was modified by the affect of heating with silver ions in the Muffle oven. Porosities were formed on the surface area and ZnSe were transformed to Ag_2Se. After ion exchange of crystal, the band gap value decreases 1.1eV.

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