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Impedance spectroscopy (IS) and thermally stimulated discharged current (TSDC) studies on CdSe-PVA nanocomposites prepared by ultrasound- assisted method

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In the present work, dielectric properties and relaxation process of the CdSe-PVA nanocomposites have been studied using Impedance Spectroscopy (IS) and Thermally Stimulated Discharged Current (TSDC) methods. The temperature dependence of conductivity, dielectric constant and dielectric loss have been studied in temperature range of 298 K to 498K and frequency range from 200Hz to 1MHz. It was found that the nature of polarization processes in pure PVA and CdSe-PVA nanocomposites are different.

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1. Introduction

The fabrication of II-IV semiconductor nanoparticles embedded and/or formed in polymeric network has been attracted much interest due to their interesting physical properties and possibility of arranging them for developing nanodevices [1-4]. As one of the most important II-IV semiconductors, CdSe in known as a tunable band gap semiconductor is a prespective candidate for the fabrication of optoelectronic devices such as photoelectrochemical cells[5-7] large screen liquid crystal display [8], light-emitting diodes [9] thin film transistors [10], fluorescent probes in biological imaging [11] , photovoltaic devices [12] gamma ray detectors [13], lasers [14], biomedical tags [15], photoconductors [16,17] etc. An important field of interest for semiconductor nanoparticles is their incorporation within polymers. In fact inorganic–organic nanocomposite-based devices can be processed with consequent control over different electro-optical properties [18].

Polymers are also excellent host materials as capping agent and stabilizer since they prevent aggloromation and precipitation of the particles. Polymer based semiconductors are also advantageous from point of view of film preparation. The embedding of such semiconductor nanoparticles polymer matrix can be consider as potential candidates for their use in electronic and optoelectronic devices. Recently, various methods to fabricate such composite films, especially polymeric films containing nanoparticles, have been reported and their electrical and oprical properties have been studied by many researchers [19-22].

Among used polymers, polyvinyl alcohol (PVA) is an important polymer having a high dielectric strength(>1000kV/mm), good charge storage capacity and dopant dependent electrical and optical properties [23].

The study of the dielectric relaxation processes in polymer nanocomposites is a useful tool to learn electrophysical characteristics of these materials. The experimental methods usually employed for this analysis are Thermally Stimulated Depolarization Currents (TSDC) and Impedance Spectroscopy (IS). These methods are powerful tools for identifying and characterizing relaxation processes of materials used by many researchers [24,35].

The electrophysical and dielectric properties of semiconductor nanocomposites has not been reported so far.

In this paper, we applied ultrasound-assisted method for preparation of CdSe monodispersed nanopowders and then have been mixed with polymer (polyvinyl alcohol) by simple dipping method on an ordinary glass slide and the electrophysical properties of CdS-PVA nanocomposites in the film form have been investigated using IS and TSDC methods.

2. Materials and methods for impedance spectroscopy

CdSe nanocrystalline powder was prepared by an ultrasound-assisted method and the structural, optical, compositional and morphological properties of samples were reported in our previous reports [36, 37]. All chemicals obtained from Merck and were used without further purification. In a typical procedure for preparation CdSe-PVA nanocomposites, 10 ml of 0.2M aqueous solution of cadmium acetate dehydrate, 10ml of aqueous solution of PVA (10%) and 10 ml of aqueous solution of 1.1M sodium selenosulfate were separately prepared in different flasks. Then all of these materials were simultaneously mixed is a rounded bottom flask and kept under ultrasonic irradiation for 1 hour. After sonication, the solution was rinsed in ultrasonic bath for remove weak bounded materials and get pure materials. For separation a centrifuge with 4000r/min where used each rinsing process. In order to preparation film CdSe nanocomposite the prepared nanopowders were add again in 10 ml of 10% PVA solution in water and kept under ultrasonic irradiation for 30 minute again to obtain homogeneous distribution in surface and volume of composite material as possible. Then a drop of viscous CdSe-PVA nanocomposite were dispersed on an ordinary microscope glass and let to dry at room temperature for electrical characterization.a thin layer silver paste was coated on both sides of prepared sample for dielectric measurement. Then the sample was located between metal electrodes as sandwich method. Thickness of film was measured by mechanical micrometer and was 100 micrometer.

The dielectric properties of CdSe-PVA nanocomposites were measured in the frequency range 200Hz – 1 MHz and temperature range between 298 K – 498 K using Immitansa (E7-20) Impedance spectrometer and the temperature was adjusted and measured Keithley system electrometer 6514.

The dielectric constant of CdSe-PVA nanocomposite was calculated from equation:

$$C = \frac{\varepsilon\varepsilon_0 S}{d}$$

where, C is capacitance, ε is dielectric constant, d is the thickness of film ε_0 is the vacuum permittivity and S is the area of used electrodes.

The ac resistance is given by:

$$R = 1 \Big/ (\omega C \tan\delta)$$

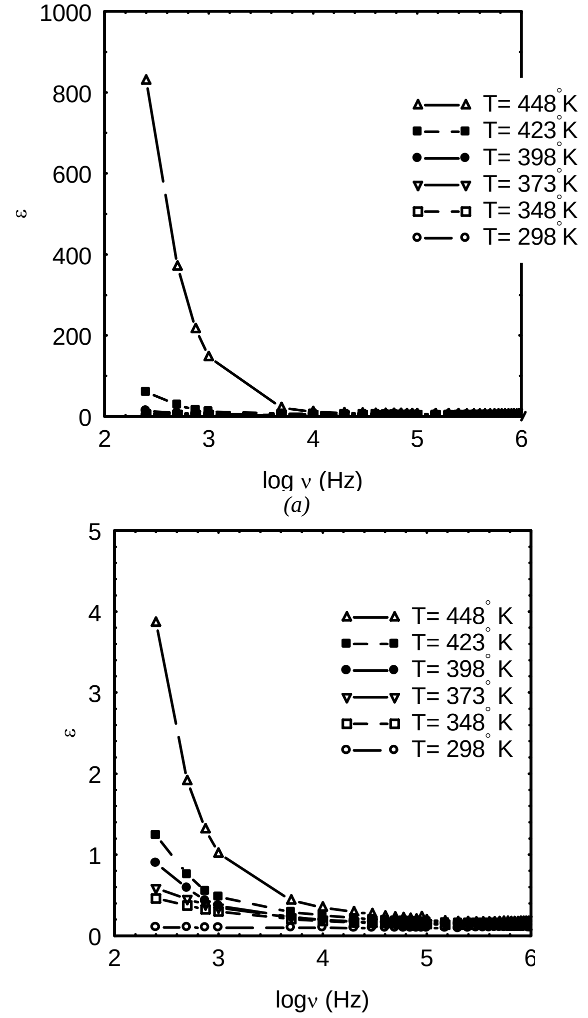
where ω is the angular frequency and C the capacitance of the sample in Farad. The real part of ac conductivity σ_{ac} was calculated as:

$$\sigma_{ac} = t \Big/ (AR)$$

where t is the thickness of the sample in cm and A the cross-sectional area in cm^2. The real part of dielectric constant ε' was calculated as:

$$\varepsilon' = (tC) \Big/ A\varepsilon_0$$

From Fig. 1 (a) and (b) it is seen that the values of dielectric constant decreases with increase of frequency at all temperatures in both cases(pure PVA and CdSe-PVA nanocomposite). The observed nature in relaxation character is due to the inability of dipoles orientation by alternating electrical field. The increase in values of permittivity with temperature is connected with the increasing of intensity rotation prosesses of dipoles. This means that the increase of temperature allows rapidly rotate of dipoles.



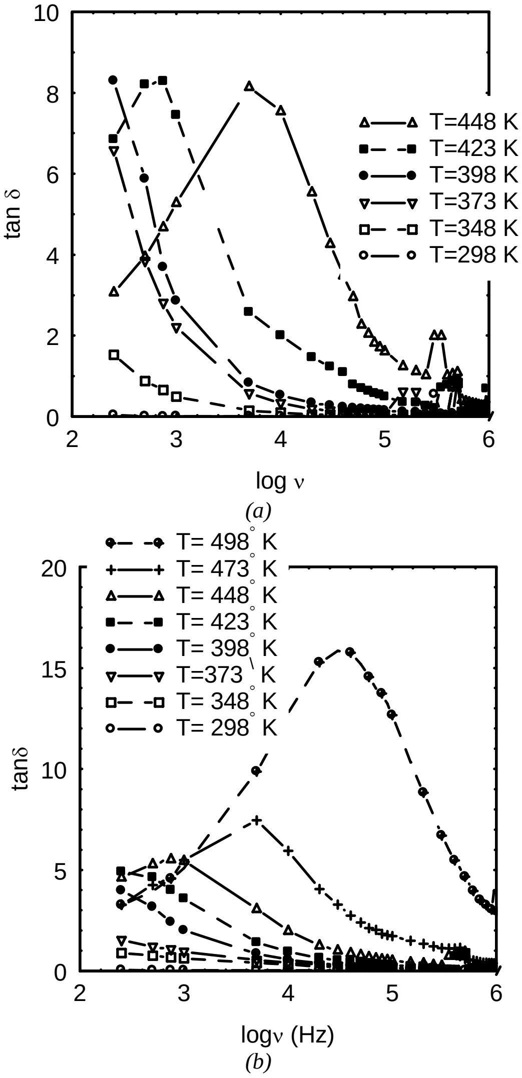
(a)

(b)

Fig. 1. (a) Temperature and frequency dependence of dielectric constant for pure PVA; (b) CdSe/PVA nanocomposites.

Fig. 1 (a) and (b) also shows that the value of permittivity of CdSe at 298 K temperature is about 11,51 and this value for pure PVA at the same temperature and frequencies are 2,65. Figures clearly show that the value of dielectric constant in CdSe-PVA is higher than its value in pure PVA. But the rate of increasing by varying of temperature and also frequency for CdSe/PVA nanocomposites being larger than pure PVA. The value of dielectric constant of pure PVA which increased from 2.6589 to 60,1945 at temperature range 298 to 423 K at 250 Hz and also the value of ε for CdSe-PVA nanocomposites in the range of 11.51 to 1381 at 250 Hz. The rate of increase of dielectric constant in both of temperatures and frequencies indicates of CdSe-PVA nanocomposite is noticeable. In this case too possible reasons are considerable. The first in the present of CdSe nanoparticles, the conductivity of sample increased and second the influence of existence of small particles can affect on energy shift in band structure of sample. The result of this process is affect on the conductivity of samples.

Fig. 2 (a) and (b) shows the variations dielectric loss with logν. Dielectric loss of PVA has a small value at temperature 298 K and it decreases with frequency and increases with temperature from 298 to 429 K. In the case of CdSe-PVA the rate of variation being smaller than pure PVA.



(a)

(b)

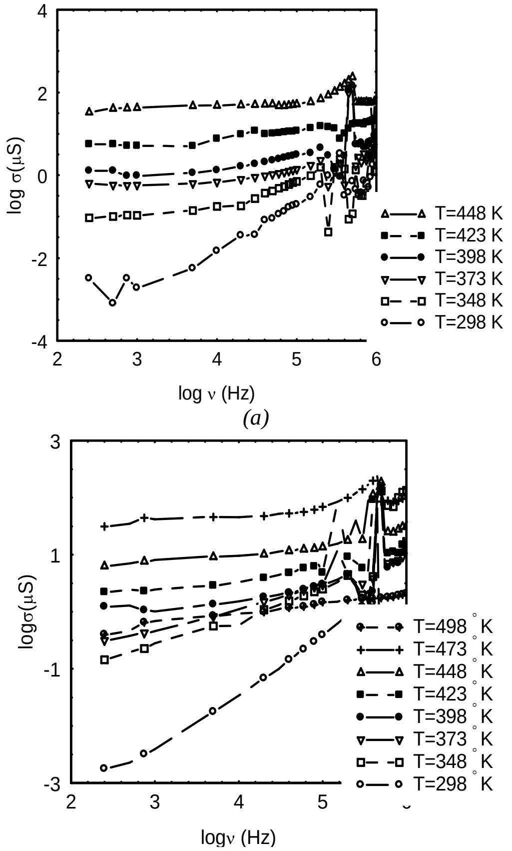
Fig. 2. (a) Temperature and frequency dependence of dielectric loss for pure PVA; (b) CdSe/PVA nanocomposites.

At lower frequency permittivity is expected to be higher due to the presence of all the different types of polarizations (interface, dipole, ionic, atomic, electronic etc.) the dielectric constant increases with rise in temperature for all the frequencies.

The rate of variation in dielectric loss of CdSe-PVA nanocomposite is smaller than pure PVA.

In Fig. 2 (a) and (b) dielectric loss pick is observed around (logν=4 Hz) at 423 K which shifts toward lower frequency regime as temperature goes down by increasing of temperature, the motion of charge carries become easier and thus can be relaxed even a higher frequency. But some of peaks is not observed at lower temperatures appear at lower frequencies, that's way they don't seen in measured frequency regions. The calculated value of relaxation time (t) using t=1/ω, was found to be $0{,}318*10^{-4}$ sec for CdSe-PVA nanocomposites at the temperature 423 K. In the case of pure PVA only one peak was observed at 423 K and the relaxation time was $0{,}207*10^{-3}$ sec. The conductivity of polymer nanocomposites were increased with temperature this expression arise of observed in decrease in dielectric loss. Comparison at same temperatures for both samples shows that the relaxation time in CdSe-PVA nanocomposite are shifted to.

Fig. 3 (a) and (b) shows that the conductivity (σ) of both of samples is found to increase linearly with frequency. σ increases at a low rate with temperature initially and more rapidly in higher temperatures. Comparison of two figures a, b shows that at a given temperature and frequency, conductivity of pure PVA is less than CdSe-PVA nanocomposites.

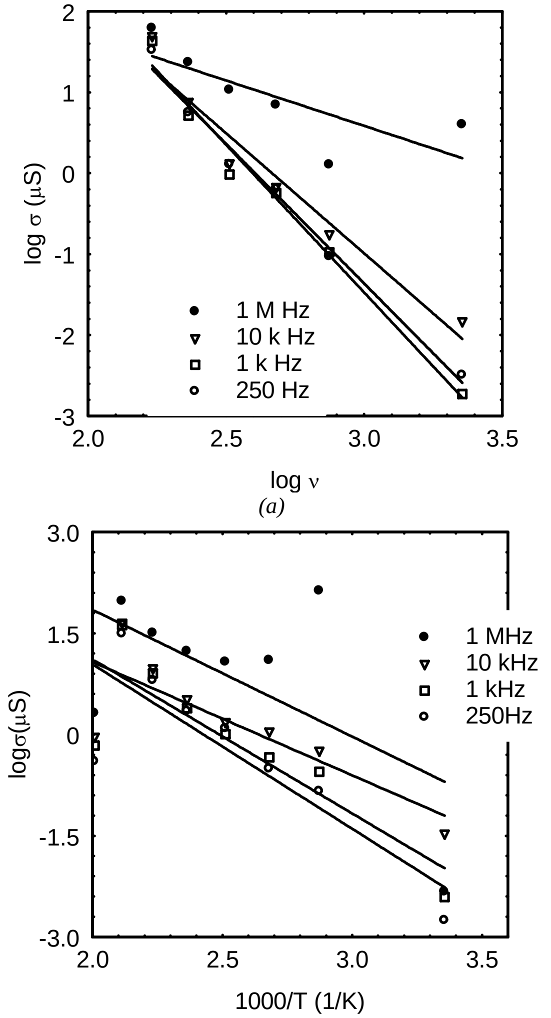


(a)

(b)

Fig. 3. (a) Temperature and frequency dependence of electrical conductivity for pure PVA; (b) CdSe/PVA nanocomposites.

The activation energy for CdSe-PVA and pure PVA was calculated from Arrenius equation and was 0,51645 and 0,77 respectively are shown in Fig. 4 (a) and (b).



(a)

(b)

Fig. 4. (a) Temperature dependence of electrical conductivity for pure PVA; (b) CdSe/PVA nanocomposites in different frequencies.

3. Characterization of polarization processes in PVA and CdSe-PVA nanocomposite by thermally stimulated depolarization method

The samples, supplied with suitable electrodes in a sandwich configuration, are heated up to a temperature T (polarization temperature) of 373 K. Then, an electric field E (polarizing field) of 10 kV/cm is applied to the sample for a time t (isothermal polarization time) of 60 minutes. After this, the samples is cooled and subjected to the TSDC measurement.

The aim of this work was to study the electrical polarization and relaxation phenomena in PVA and CdSe-PVA nanocomposite to better understand these processes. Special attention was paid to the influence of addition of CdSe nanocrystals to PVA matrice.

Two samples, pure PVA and CdSe-PVA nanocomposites, and with respectively 80, 120 micrometer thick in the film form were prepared by mixing CdSe nanopowder in aqueous PVA. The CdSe nanopowder used for this experiment was synthezied by sonochemistry method in our previous work [36].

Circular aluminum electrodes of 10mm diameter were kept on both sides of all samples. Characterization of samples were performed using an electrometer, Model y5-11 from Russia, sample chamber and a plotter, model H306, Russia.

Thermally stimulated depolarization currents spectrum of the PVA and CdSe-PVA nanocomposite has been analyzed by inducing polarization temperature from room temperature to about 460 K. The rate of increasing in temperature in all experiment was 5K/min. In both samples relaxation peaks observed. In the case of pure PVA, Fig. 1 show three TSDC curves of polarized same sample for three times. The first (I) is related to the first polarization. It shows that a small shoulder at temperature 433 K. it is connected with the destruction of the crystalline phase in PVA. Then the sample was polarized and cooled at 373 K for two times again and the plot of relaxation process from TSDC technique were shown in Fig. 5 (II and III).comparison between second and third polarizations shows the first peak in both curves are in same values and covers them. Comparison of these peaks also shows that, second polarization is shifted to higher temperatures. There are some possibilities for this observation; the most probable reason for this observation is change from amorphous to crystalline phase for PVA polymer. It is clear that the orientation and reorientation of dipoles are appears due to PVA are a highly polar polymer. This observation also connected with the polarity of the PVA. This is due to increasing in crystalline phase in PVA. It is clear that in third polarization the crystalline phase is relatively more in pure PVA in comparison with the second polarization for same sample. Shift in the value of temperature is a result of this expression. The reason of increasing in crystalline phase has a connection with increasing the interface area in amorphous and crystalline phase. It means that the charges between interfaces were increased. In the case of CdSe-PVA nanocompoites, the relaxation takes place in the crystalline-amorphous interface. In this case crystalline CdSe particles in nanoparticle-polymer interfaces. The analysis reveals two changes in peaks at different temperatures for each polarization. For first polarization the peak were formed at about 403K and for second polarization the peak shifted to lower temperatures.

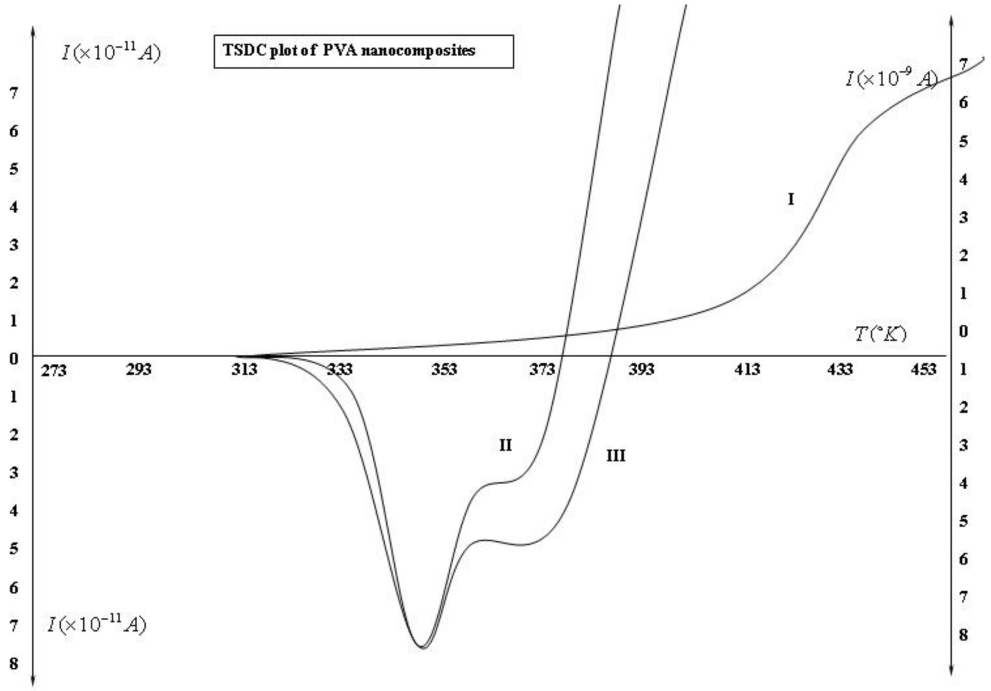


Fig. 5. TSDC plot of PVA polymer.

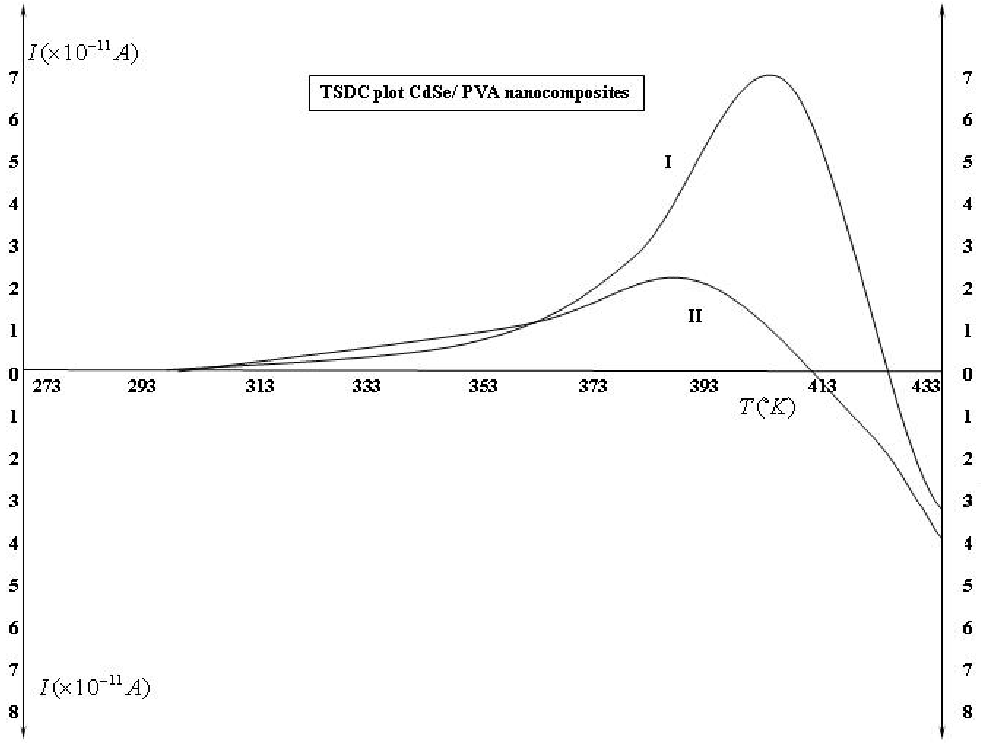


Fig. 6. TSDC plot of CdSe/PVA nanocomposites.

Fig. 6 shows that the polarization process in CdSe-PVA nanocomposites are different with comparison in pure PVA. As shown in Figs. 5 and 6, it is possible to say that collected charges at interface in the case of CdSe-PVA nanocomposites are in the opposite side of pure PVA. Also the magnitude of maximum in the second polarization is low. All of these observations have direct connection with occurred processes at interface of polymer and nanoparticles. The changes in degree of crystallinity are the most probable process. In the second polarization the interface between phases were increased and defects were decreased, it is because of decreasing in collected electrical charges, but the structure have more amorphous phase in the first polarization.

4. Conclusions

In conclusion, the experiments of IS and TSDC analyses show that, polarization process in pure PVA and CdSe-PVA nanocpmposites are different. In this case, occurred processes at interface of polymer nanoparticle play a key role for descriptions of these processes. The dielectric constant decreases with increase of frequency at all temperatures for both PVA and CdSe-PVA nanocomposite. The values of dielectric constant in CdSe-PVA nanocomposite are large and are connected to small size of CdSe particles

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