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Light absorption process in CdS_xSe_{1-x} doped alumino-phosphate glass

A. STANCULESCU[*], F. STANCULESCU[a], M. ELISA[b]
National Institute of Materials Physics, Bucharest, Romania
[a]*University of Bucharest, Faculty of Physics, Bucharest, Romania*
[b]*National Institute for Optoelectronics, Bucharest, Romania*

We present a study of the effect of the crystallites composition and size on the optical properties of vitreous aluminophosphate matrix doped with CdS_xSe_{1-x} crystallites. The influences of the glass matrix composition and, heat treatment temperature and duration on the stoichiometry of the crystalline phase have been investigated by optical methods. We have studied the effect of the sodium oxide contained in the matrix, annealing temperature variation from 425 °C to 475 °C and duration variation from 2 h to 6 h on the light absorption process, evaluating an optical band gap energy between E_g=1.74 eV and E_g=2.29 eV associated with changes in the composition of the crystallites. The blue shift of the absorption edge observed in samples containing Na_2O annealed at 425°C for 4 h or at 450°C for 2 h was attributed to a variation in the crystallites' composition because their size is not favourable to the quantum confinement. We have also investigated the effect of individual CdS and CdSe clusters on the absorption properties of the aluminophosphate glass and on the process of zinc incorporation in the crystalline phase. We have made some assumptions concerning the effect of the aluminophosphate glass matrix on the direct band to band light absorption mechanism characterising the II-VI bulk semiconductor.

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1. Introduction

In the field of materials for optical applications, an increased interest has been shown lately to a special class of composite materials: semiconductor doped glasses [1-5]. In these systems the crystallites are grown directly by precipitation in a transparent glassy host material [6]. When the crystallites have dimensions of tenth of nanometers, dimension effects are not present and this material can be used as colour, yellow to red, "sharp-cut" filters because the absorption edge shifts, depending on the composition [1]. For dimension of the crystalline phase close to the radius of the Bohr exciton characteristic for the corresponding bulk semiconductor, are present quantum confinement effects generating a non-linear optical behaviour of the material [7-9].

Semiconductor doped glasses can be used to the fabrication of integrated optical structures, optical circuits with fast switching time (below 10^{-14} s), planar channel wave guides, optical modulators, electro-optical switchers [10-13]. The greatest disadvantage of this composite material is the relatively low efficiency of the optical non-linear phenomena compared with those in bulk semiconductors.

If harmonics generation and parametrical phenomena are important in optical non-linear crystalline systems, optical bistability is characteristic for vitreous systems [14]. Compared with the spectra of ions doped glasses that are characterised by broad absorption bands in the UV, visible and IR [15], spectra of semiconductor-doped glasses show an edge of the fundamental absorption at a special wavelength, indicating a band-to-band absorption process as in semiconductors [1].

In the last years most research has be done on silicate [16-22] or borosilicate [23-25] glass matrices containing a microcrystalline phase of II-VI binary (CdS, CdSe) or ternary CdS_xSe_{1-x} compound.

Because a way to modify the optical properties of the composite material could be the change of the glass matrix composition, another research direction is represented by CdS_xSe_{1-x} semiconductor doped alumino-phosphate glass [26-30].

The glass composition and the thermal regime parameters such as temperature and duration determine the dimension (nucleation and growth rate) and composition of the crystalline phase and so the optical linear and non-linear properties.

2. Experimental methods

The most important problem in the preparation of semiconductor doped glasses is the difficulty to obtain a high concentration of semiconductor crystallites in the glass because of the low solubility of semiconductor in the melted glassy matrix and high volatility of the chalcogenides at the temperature of the glass formation. The concentration of the semiconductor increases in phosphate based glass matrix because the solubility of chalcogenides increases [31]. Composition of the glass is also very important for reducing the loss of semiconductor through evaporation. To avoid these phenomena we have chosen a glass matrix with a batch melting and preparation temperature ~ 1200 ^oC, with 400 ^oC less than this temperature for silicate glasses.

We have investigated three categories of samples prepared using three different compositions for the glass matrix:

Li_2O-P_2O_5-Al_2O_3-BaO -La_2O_3 with 1 wt% $CdS_{0,5}Se_{0,5}$ and 1 wt% ZnO -sample P1,

Li_2O-P_2O_5-Al_2O_3-BaO-SiO_2-La_2O_3 with 1 wt% $CdS_{0,5}Se_{0,5}$ and 1 wt% ZnO-sample P2,

Li_2O-Na_2O-P_2O_5-Al_2O_3-BaO-SiO_2-La_2O_3 with 1 wt% $CdS_{0,5}Se_{0,5}$ and 1 wt% ZnO-sample P3,

the amount of the matrix components (LiO_2, P_2O_5, Al_2O_3, BaO, La_2O_3) being calculated using the molecular formula of the glass.

Around 200 ^oC were simultaneously generated lithium, sodium, barium and aluminium phosphates and for the homogenisation of the phosphates mixture the batch was dried at 120^{o}C and the result was then thermally treated at a temperature between 700-800^{o}C. In the next step, the glass was molten around 1200^{o}C and outgased for a few hours to prepare a homogeneous glass free of defects and then were added the dopants.

Glass matrix composition can be changed adding small amount of Na_2O**,** which together with SiO_2 and ZnO have a positive influence on the nucleation and growth of the microcrystallites, generating the shift of the fundamental absorption edge. These oxides retain S, Se, Cd as complexed compounds at high temperature and release them at low temperature, through the generation of sodium silicate before the heat treatment, immediately after the outgasing of the molten glass and adding of cadmium, sulphur and selenium and the. This way we can avoid the formation of sulphur, selenium and cadmium oxides because the aluminophosphate matrix is strongly oxidant and favours this process.

Then, precise quantities of cadmium, sulphur and selenium, corresponding to the stoichiometric composition, $CdS_{0.5}Se_{0.5}$, were added to the molten batch of the glass matrix. The concentrations of the semiconductor phase components in the final glass can differ significantly from the initial concentration in the batch because the sulphur (T_{vap}=446^{o}C) and selenium (T_{vap}=688^{o}C) can leave the system at the melting temperature of the glass. Sulphur starts to leave the system before selenium and to counteract the loss by volatilisation we have introduced in the glass batch a supplementary quantity of sulphur to maintain the sulphur/selenium ratio that corresponds to the stoichiometric composition x=0.5 of the CdS_xSe_{1-x} crystallites [32].

After the casting process, the colourless and transparent glass was annealed in an isothermal treatment furnace at different temperatures (425^{o}C; 450^{o}C; 475^{o}C) for different time periods (2 h; 4 h; 6 h) to assure the nucleation and growth of the microcrystallites through the precipitation from a supersaturated solid solution [26] in a process implying the following steps: 1. nucleation (germination) of the crystallites when increases the number of particles with constant size, equal to the critical radius; 2. growth of the crystalline phase on the account of the dissolved Zn, Cd, S, Se diffusion towards these nuclei; 3. growth of the precipitates critical radius with the decrease in the amount of reactants in the glass matrix, leading to Lifshitz-Slyzov ripening, when most of Zn, Cd, S, Se ions are in crystallites and the largest crystallites are grown on the account of the dissolution of the smaller ones [16,24,25]. The grown semiconductor crystallites are randomly distributed in the glass matrix and their radius (R) increases with the heat treatment duration (t), for a given temperature, accordingly to the Lifshitz-Slyozov relation: $R \cong t^{1/3}$ [33,34].

The development of the crystalline phase by heat treatment leads to the colouring of the glass [1,35]. The annealing temperatures (≤ 475^{o}C) were below the transition temperature for alumino-phosphate glass [31,36-38] and less than those used for silicate glass, which exceeds 600 ^oC [16]. The thermal treatment also increases the homogeneity of the sample, resulting a stress-free glass of good optical quality.

More details concerning the manufacturing process of these semiconductor-doped glasses were given in previous papers [26,27,39].

The samples mechanically polished, with optically processed surfaces have been investigated by UV-VIS spectrophotometrical methods using a computer assisted SPECORD M-42 apparatus.

3. Results and discussion

The aim of our study is to analyse the influence of glassy matrix composition and of the heat treatment temperature and duration, on the particularities of the light absorption process in semiconductor-doped aluminophosphate glasses. From the position and the shape of the fundamental absorption edge we have obtained information on the microcrystalline phase growth and deduced some intrinsic properties of the material, as the optical band gap energy.

The reference glass matrices with compositions corresponding to P2 and P3 were transparent in the all visible spectral range, 319-800 nm respectively 258-800 nm and their transparency changed by doping and annealing, indicating the generation of the microcrystalline phase.

From previously preliminary investigations [40] has been evidenced the influence of the temperature and duration of the heat treatment on the position of the fundamental absorption edge. This paper presents a study of the correlation between the shift of the absorption edge (Table 1) and the composition for “big” size CdS_xSe_{1-x} crystallites.

All the absorption spectra at room temperature for the sample P2 and P3 treated at different temperature (425^{o}C, 450^{o}C or 475^{o}C) for 2 h, 4 h or 6 h show no additional peaks (Figure 1 and Figure 2). The formation of this absorption peak and its shift towards high energy after the heat treatment could be associated with the absorption of light by semiconductor nanoparticles in glass, corresponding to the optical transition between the first quantum confined levels $E_{01}^{h} \rightarrow E_{01}^{e}$ and indicating the strong confinement of electrons and holes in the matrix [25].

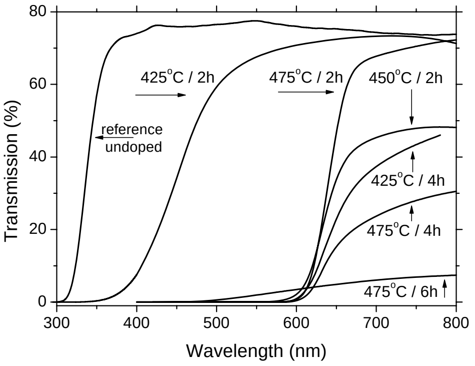

Fig. 1. Fundamental absorption edge shift for P2 samples at different temperature (425°C, 450°C and 475 °C) and different duration (2 h, 4 h and 6 h) for the heat treatment.

The absence of the quantum transition peak in our spectra is due to the big size of the crystallites and not to their wide distribution as was confirmed by transmission electron microscopy measurements. The crystallite size evaluated by TEM for sample P2 annealed at 475 °C for 6 h and sample P3 annealed at 475°C for 2 h varied between 0.3-0.9 μm [39].

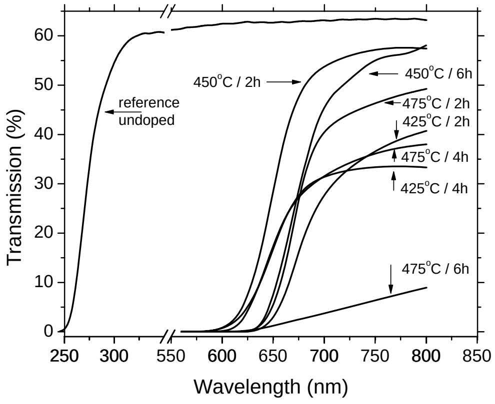

Fig. 2. Fundamental absorption edge shift for P3 samples at different temperature (425oC, 450°C and 475 °C) and different duration (2 h, 4 h and 6 h) for the heat treatment.

The annealing process can change the composition of semiconductor phase in our systems. For high temperature heat treatment it is expected an increase in the sulphur content in the crystallites because is favoured the sulphur incorporation in crystallites while the selenium has the tendency to remain in the glass. The shift of the fundamental absorption edge is associated with changes in the band gap energy determined by the increase/decrease in sulphur content generating variations in semiconductor particles composition.

The red shift of the fundamental absorption edge obtained increasing the temperature of the thermal treatment can be associated with a material containing big size crystallites with a low content of sulphur.

The blue shift of the fundamental absorption edge can be determined by particle size, compositional changes or strain. The absence in the absorption spectra of the thermally treated samples of a peak situated at lower energy than the absorption edge makes less probable the manifestation of quantum confinement effects [32].

In sample P2, with the composition presented above, we have observed an increase in the shift between the absorption edge in doped glass and the glass matrix, from $\Delta\lambda_g$=72 nm to $\Delta\lambda_g$=292 nm (Table 1), when the temperature increases from 425°C to 450°C for the same duration, 2 h of the annealing (Figure 1). This increased red shift is associated to an increase in the crystallites' size or to the development in the glass of crystallites with low content of sulphur.

The subsequent increase of the annealing the temperature from 450°C to 475°C practically have no influence on the position of the absorption edge (Table 1) indicating no significant changes in the composition or dimension of the crystalline phase (Figure 1).

In sample P3 we have remarked an important blue shift of the absorption edge in doped glass compared to glass matrix from $\Delta\lambda_g$=398 nm to $\Delta\lambda_g$=361 nm (Table 1) with the increase of the temperature from 425°C to 450°C for the same duration of the heat treatment, 2 h (Figure 2) which can not be associated with quantum confinement effects. We propose, as the dominant process generating this shift, the modification in the crystallite composition by the incorporation of the sulphur favoured by the presence of sodium oxide in the glass matrix. Increasing the temperature to 475°C the shift has reduced (Figure 2) because the crystallite composition has changed. The quantity of sulphur incorporated in crystallite at higher temperature (475°C) decrease, being only partially released by sodium oxide.

We also have investigated the effect of the annealing duration on the characteristics of the crystallites (composition, dimension) developed at different temperatures in different glass matrix.

For the same temperature of the heat treatment (425°C), an increase in the duration of the heat treatment from 2 h to 4 h for sample P2, has generated an increase in the red shift between the absorption edge in the composite material and the glass matrix from $\Delta\lambda_g$=72 nm to $\Delta\lambda_g$=298 nm. An equal shift has been obtained, as presented above, for the same duration, 2 h, and an increase in the temperature of the heat treatment from 425°C to 450°C and can be correlated with smaller dimension or lower content of sulphur because in this matrix the transport of the semiconductor components to the nuclei is less efficient. A significant reduction in this red shift in sample P2 appeared for a temperature of 475°C increasing the duration of the annealing from 2 h to 4 h.

A blue shift of the absorption edge is obtained in sample P2 for 475°C and 6 h heat treatment (Fig. 1). In the sample with no sodium oxide in the composition, the incorporation of sulphur is more important at higher temperature (475°C) and long time heat treatment because bigger quantities of sulphur diffuse to the nucleation site, justifying the blue shift.

We have observed in sample P3 (Figure 2), for a given temperature 425°C or 475°C and an increase from 2 h to 4 h in the duration of the heat treatment a decrease in the shift between the absorption edge in doped glass and glass matrix from $\Delta\lambda_g$=398 nm to $\Delta\lambda_g$=305 nm respectively from $\Delta\lambda_g$=391 nm to $\Delta\lambda_g$=369 nm (Table 1). In sample containing sodium oxide sulphur remains partially captured by it and the blue shift decreases at higher temperature (475°C) and long duration (6 h) of the heat treatment (Figure 2).

At long time thermal treatment (6 h) the smooth slope shape of the absorption edge in both sample P2 and P3 (Figure 1 and Figure 2) indicates a distribution after dimension of the crystallites in the glassy matrix while the steep shape for short time thermal treatment (2 h and 4 h) indicates a specific dominant dimension of the semiconductor crystallites [34].

We have emphasised that the crystalline phase composition is determined beside the temperature and duration of the heat treatment, by the glass matrix composition.

Raman spectroscopy preliminary investigation [39] offered complementary information on the variation in composition of the CdS_xSe_{1-x} crystallites developed, for example, in sample P2 annealed at 450°C for 2 h and sample P3 annealed at 450°C for 6 h. Because this compound is know as “two-mode behaviour” alloy [25] the first order Raman spectra indicate the simultaneous presence of the optical vibration modes (LO) characteristic for the binary compounds: 296 cm^{-1} for CdS and 200 cm^{-1} for CdSe [39]. A variation of the intensities ratio of CdS and CdSe like modes (I_{CdS}/I_{CdSe}) indicates a decrease in the content of sulphur in the crystallites developed in sample P3 annealed at 450 °C for 6 h compared to sample P2 annealed at 450 °C for 2 h, as was deduced from the red shift of the absorption edge in these samples.

We also have studied the fundamental (intrinsic) absorption edge in CdS_xSe_{1-x} semiconductor doped aluminophosphate glass to evaluate the optical band gap of the composite material, which is correlated with modification in crystallite composition.

We have processed the experimental transmission data using a power function:

$$\alpha(E) = A + B \cdot (E - C)^D \qquad (1)$$

where $\alpha[cm^{-1}]$ is the absorption coefficient, C[eV] is the band gap energy, E_g, D is an dimensionless coefficient correlated with the absorption mechanism and $A[cm^{-1}]$, $B[cm^{-1}]$, are constants. We use a power function because this corresponds to classical absorption mechanisms with power dependence for direct and indirect transitions (“1/2” exponent for direct allowed transitions, “3/2” exponent for direct forbidden transitions and “2” exponent for indirect transitions). Examples of interpolations for sample P2 and P3 are given in Fig. 3a and 3b.

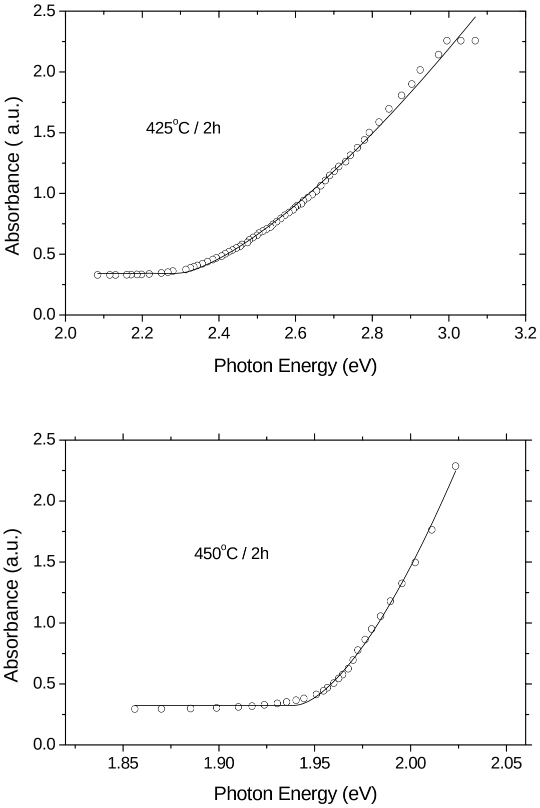

Fig. 3. a) Experimental data fitting using function (1) for a P2 sample treated at 425°C for 2 h. b) Experimental data fitting using function (1) for a P3 sample treated at 450 °C for 2 h.

We have obtained for the band gap energy values between 1.74 eV corresponding to the binary compound CdSe [41] and 2.29 eV (Table 2), depending on the glass matrix composition and heat treatment conditions, and a coefficient D, associated with the absorption mechanism, between 1.49 and 3.89. The heat treatment has led in our sample to a change in the band gap energy, determined by variations in the composition of the microcrystallites caused by changes in sulphur content.

In sample P2 (with no natrium oxide) an increase in temperature from 425 °C to 475 °C for the same duration, 2 h, of the heat treatment has generated an important change in the absorption mechanism, from direct to indirect transition (Table 2), and decrease in the band gap energy from E_g=2.29 eV to E_g=1.99 eV, related to the red shift (Figure 1) of the fundamental absorption edge explained by the inefficient sulphur transport through the germination site even at high temperature, in the absence of sodium oxide.

A consequence of the large size crystalline phase development is an increase in the local strain in the individual crystallites due to the thermal expansion mismatch between the semiconductor clusters and the host medium. In our system II-VI crystallites/vitreous matrix this effect is not too strong because the glass contracts faster than the crystallites while cooling down from the preparation temperature [42]. More important are the growth defects in the crystallites causing local rearrangement of the atoms [42-44] and generating a significant deviation from the normal direct gap semiconductor behaviour of CdS_xSe_{1-x} crystallites in P2. The light absorption mechanism change (Table 2) from direct non-allowed transition (D=1.60) to allowed indirect transition (D=2.23).

In sample P3, an increase in temperature from 425°C to 475°C for the same duration, 4 h, of the heat treatment has led to an increase in the band gap energy, from E_g=1.74 eV to E_g=1.80 eV in concordance with the blue shift of the fundamental absorption edge (Figure 2). This confirms, accordingly to [16], an increase of the sulphur content in the microcrystallites because, as we have discussed above, there is no evidence of the quantum size effects and of the electrons and holes confinement in these particles. Changing the thermal regime by increasing the temperature from 450°C to 475°C for the same duration, 2 h, (Table 2) we have remarked the red shift of the fundamental absorption edge associated to a decrease in the band gap energy from E_g=1.95 eV to E_g=1.85 eV showing a lower sulphur content in crystallites, because the sulphur captured by sodium oxide is only partially released and diffuses to nucleation sites to be incorporated in crystallites. Light absorption by direct non-allowed transitions (D=1.49) characterize the sample P3 annealed at T=450°C for 2 h and corresponds to the biggest blue shift (Figure 2). Changes in the absorption mechanism from D=1.49 (direct transition) to D=2.45 (indirect transition) have also been emphasised increasing the temperature to 475°C for the same duration (2 h) of the heat treatment. At a given temperature, 475°C, the deviation from this mechanism increases (D=3.63) with the increase in the heat treatment duration to 4 h, because the strain in the crystallite increases. The strongest deviation from the direct transition (D=3.89) is observed in sample P3, annealed at lower temperature, 425°C for 4 h.

We have prepared special samples from the reference glass matrix with composition P3 doped with 1 wt% CdSe and 1 wt% ZnO, respectively 1 wt% CdS and 1 wt% ZnO and annealed at 450°C for 4 h, to develop CdSe respectively CdS semiconductor crystallites. The goal was to study the effect of the crystalline binary II-VI semiconductor compounds on the optical absorption in the aluminophosphate glass matrix. Deviation of the band gap energy of this composite material from the theoretical values associated with the bulk semiconductor, CdSe and CdS, are attributed to the extern perturbation generated by the glass matrix that affect the energetic levels of the semiconductor crystallite [42].

The fundamental absorption edge in undoped P3 aluminophosphate glass matrix is situated at 258 nm. In CdSe doped glass matrix there is no evidence of the incorporation of Zn from the matrix into the crystallites and formation of the ternary compound $Cd_xZn_{1-x}Se$ because the position of the fundamental absorption edge and as a consequence the optical band gap energy are not situated between the value E_g=1.74 eV for CdSe and E_g=2.58 eV for ZnSe [45].

This type of glass is rich in cadmium and is no need for Zn to enter the crystallite because selenium has the tendency to remain in glass. For CdSe doped glass, the value (E_g=1.57 eV) for the band gap energy obtained by fitting the absorption data with function (1) (Figure 4), is far from the value corresponding to the hexagonal bulk semiconductor compound at 300 K (E_g=1.74 eV). This red shift of the absorption edge could be generated by the hydrostatic component of the compressive strain exerted by the host medium on the semiconductor microcrystallites [43,46] suggesting a pressure of tenth of kbar and a possible phase transition from hexagonal CdSe to salt-rock CdSe crystallite [46]. The steep, rather non-structured (featureless) absorption edge is similar to optical transition characteristic for bulk crystal, supposing that CdSe centers are ‘big” crystallites surrounded by a dielectric medium (glass). The existence of this strain in this crystallite is confirmed by the large deviation from the normal direct band-to-band absorption mechanism (D=3.56 correspond to an indirect forbidden transition).

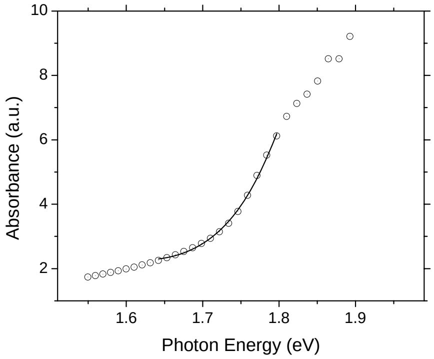

Fig. 4. Experimental data fitting for the glass matrix corresponding to a P3 sample doped with CdSe crystallites.

More probable seems to be the incorporation of Zn in CdS crystallites in aluminophosphate glass. This process has been studied till now only in a silicate glass matrix [23,24].

The process of microcrystallites generation and their stoichiometry in CdS-doped glass are influenced by the presence of zinc in the glass matrix that can substitute Cd atoms in a certain measure that leads to a decrease in the average lattice constant of the crystallite [21,24,45], and determine an increase in the band gap energy (Figure 5).

The value of the optical band gap, E_g=3.66 eV, situated between the values E_g=2.53 eV for hexagonal CdS [45] and E_g=3.74 eV for hexagonal ZnS [45], suggests the generation of semiconductor crystallites with a composition which varies with that of the solid solution $(ZnS)_x(CdS)_{1-x}$.

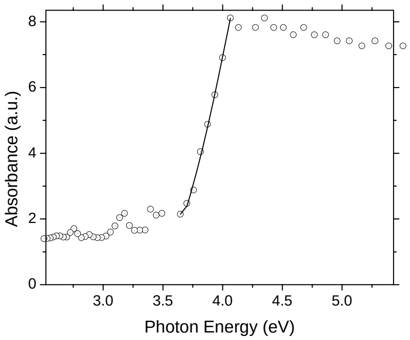

Fig. 5. Experimental data fitting for the glass matrix corresponding to a P3 sample doped with CdS crystallites.

The spectrum has a structured feature with peaks situated at 2.76 eV (which is 0.23 eV above the gap for bulk CdS at room temperature), 2.88 eV, 3.18 eV and 3.40 eV (which is 0.34 eV below the gap for bulk ZnS at room temperature). This last peak, a shoulder of the absorption edge in the low energy side could be attributed to the first excitonic absorption in $Zn_xCd_{1-x}S$.

The position of the fundamental absorption edge in this sample (λ_g=339 nm) is related to a determined ratio between cadmium and zinc incorporated in the crystallite, the incorporation of Zn being controlled by the ratio between Zn and Cd dissolved in the glass. The fundamental absorption edge will shift through longer wavelengths with the increase in CdS content and in the constant of the lattice incorporating Zn [24]. As nucleation and growth of the crystalline phase proceeds, Cd is incorporated into particles, and the glass doped with CdS has a deficit of cadmium but increases the ratio of Zn/Cd dissolved in the glass, driving more Zn into the crystallites. Because the sulphur has the tendency to be incorporated in crystallite, during the formation of microcrystallites decreases the content of cadmium available and zinc will be incorporated in microcrystallite to allow, from thermodynamic considerations, to a greater amount of sulphur to remain in the crystalline phase.

The band gap in würtzite structure $Zn_xCd_{1-x}S$ at room temperature varies non-linear with the composition (x) [47] and can be empirically fitted by a polynomial function:

$$E_g(x)=2.45+0.705\cdot x+0.603\cdot x^2 \text{ [24]} \qquad (2)$$

Using for the energy band gap, E_g=3,66 eV, obtained from the fitting of the experimental absorption data using function (1), the crystallites composition was found to be $Zn_{0.94}Cd_{0.06}S$. Zn incorporation in crystallites is favoured by the double atomic concentration of Zn compared to the atomic concentration of Cd deduced from the given composition of the glass together with the significant lost of Cd from the system, because of its high volatility, before the beginning of the crystallites nucleation.

Confinements effects are not present in our samples of alumino-phosphate glasses containing CdS or CdSe crystallites because we have not emphasised any significant blue shift of the fundamental absorption edge in the composite material CdSe (CdS)/alumino-phosphate glass compared with the bulk corresponding CdSe or CdS semiconductor compound.

Analogously, for a better approximation of the crystalline phase composition, in the composite material II-VI semiconductor/alumino-phosphate glass, it could be possible to use a system of four components $Zn_yCd_{1-y}S_xSe_{1-x}$ instead of a three components system, CdS_xSe_{1-x}, as it was discussed in this paper.

Table 1. Absorption edge position in P2 and P3 samples in correlation with glass matrix composition and annealing conditions

Sample	Annealing conditions		Absorption edge position (nm)
	Temperature (°C)	Duration (h)	
P2 matrix			319
P2	425	2	391
		4	617
	450	2	611
	475	2	616
		4	624
		6	656
P3 matrix			258
P3	425	2	656
		4	624
	450	2	619
		6	645
	475	2	649
		4	627
		6	725

Table 2. Experimental data fitting for CdSxSe1-x doped aluminophosphate glasses using function (1).

Sample	Fitting parameters:			
	A $[\text{cm}^{-1}]$	B $[\text{cm}^{-1}]$	C [eV]	D
P2: 425 °C; 2h	0.37178	3.29615	2.28647	1.59671
P2: 475 °C; 2h	0.21305	377.18906	1.98904	2.23077
P3: 425 °C; 4h	0.45460	197.11249	1.73654	3.88981
P3: 475 °C; 4h	0.46153	818.64369	1.79733	3.62806
P3: 450 °C; 2h	0.37369	84.75277	1.94601	1.49123
P3: 475 °C; 2h	0.43486	690.76506	1.84748	2.44834

5. Conclusions

This paper presents a study of the correlation between the shift of the absorption edge and the crystallites composition and dimension in CdS_xSe_{1-x} semiconductor-doped aluminophosphate glass, taking into account the effect of the glass composition and annealing conditions.

In sample free of Na_2O, the increase in annealing temperature has generated an increased red shift correlated with the large size crystallites developed in the glass. For higher temperature and long duration of the heat treatment the transport to the nucleation site and incorporation of sulphur is more efficient justifying the blue shift.

The blue shift of the fundamental absorption edge in sample containing Na_2O with the increase of the annealing temperature is explained by changes in composition, because the oxide favours the incorporation of the sulphur into crystallites. This shift is reduced after the thermal treatment at higher temperature because the sulphur captured by sodium oxide is only partially released and the quantity of sulphur in crystallite decrease.

Processing the absorption data with a power function we have obtained a band gap energy between 1.74 eV and 2.29 eV, corresponding to modifications in the semiconductor phase composition determined by the glass matrix composition and heat treatment conditions.

The sample containing Na_2O annealed at T=450°C for 2 h shows the biggest blue shift of the absorption edge and is characterized by a light absorption by direct transitions (D=1.49). For all the other samples the deviation from this mechanism increases because the strain in the crystallite increases with the increase in heat treatment duration at high temperature in sample free of Na_2O (from D=1.60 to D=2.23) and with the increase in temperature in sample containing Na_2O (from D=1.49 to D=3.89).

By doping the glass matrix containing Na_2O with CdSe we have obtained no evidence of the incorporation of Zn from the matrix into the crystallites and the formation of the ternary compound $Cd_xZn_{1-x}Se$. The red shift of the absorption edge compared with bulk CdSe is explained by the transition to the rock-salt phase generated by the hydrostatic component of the compressive strain exerted by the glass on the semiconductor microcrystallites.

The optical band gap, E_g=3.66 eV, obtained for CdS doped alumino-phosphate glass has confirmed the generation of the solid solution $(ZnS)_{0.94}(CdS)_{0.06}$ favoured by the atomic concentration ratio between Zn and Cd in our glass matrix.

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[*] Corresponding author: sanca@infim.ro