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Optical and structural investigations on Cd-S-Se-doped aluminophosphate glasses

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Aluminophosphate glasses doped with semiconductor CdS_xSe_{1-x} crystallites were produced by a wet non-conventional method that provides a high optical homogeneity of the glass. The samples belong to the oxide systems: Li_2O-BaO-Al_2O_3-La_2O_3-SiO_2-P_2O_5 (SDG1) and Li_2O-Na_2O-BaO-Al_2O_3-La_2O_3-SiO_2-P_2O_5 (SDG2) to which we added $CdS_{0,5}Se_{0,5}$ 1 % wt. (0.9 % mol.) and ZnO 1 % wt. (1.5 % mol.). The UV-VIS-NIR transmission spectroscopy revealed the shift of the transmission edge, depending on the temperature and the duration of annealing. As a general trend, the higher the temperature and the duration of the annealing process the more significant the shift of the transmission edge to higher wavelengths in the visible range. Consequently, the glass changed from colourless to red that indicates the presence of $CdS_{0.7}Se_{0.3}$ crystallites in the vitreous phosphate matrix, as also indicated by transmission electron microscopy analysis (TEM). Raman spectra obtained by Ar^+ laser excitation at 514.5 nm, showed first and second order scattering lines from $CdS_{0.7}Se_{0.3}$. The device SPIRICON LBA 300 provided information regarding the dispersal of the crystallites in the host aluminophosphate glass. Thus, by a diode laser excitation at 625 nm, we analyzed relative intensity profile of the emergent beam from the doped-glass samples and we were able to estimate the crystallites dispersal in these vitreous materials.

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1. Introduction

II-VI semiconductors, such as CdS, CdSe, CdS_xSe_{1-x}, in nano-crystalline form (quantum dots) exhibit quantum confinement effects as the nanocrystal size approaches the exciton Bohr radius. This quantum confinement gives rise to interesting new effects and enhancement of non-linear optical properties is expected [1]. High optical quality phosphate glass heavily doped with CdS, CdSe, CdTe, ZnS nano-crystals have been recently obtained [2,3].

Glasses doped with micro crystallites of the mixed semiconductor CdS_xSe_{1-x} are of practical interest due to their optical and mechanical properties. These materials are available commercially as colour-glass (yellow-to-red) "sharp-cut" filters [4,5] and optical waveguides [6]. Glasses doped with semiconductor micro crystallites are also used in holography [7] and as temperature fibre sensor [8].

CdS, CsSe and CdTe nano-crystals are luminescent and can serve in photo-voltaic cells [9].

Recently, it was shown [10] the CdSe polycrystalline films, which are photo-conductive, are strongly influenced by thermal annealing. The adsorbate influences the photo-conductiv and photo-luminescence phenomena. These effects are also possible in amorphous matrices.

In this paper we present some optical and structural studies on two compositions of semiconductor CdS_xSe_{1-x} doped aluminophosphate glasses. We investigated the influence of the temperature and the duration of the annealing on the crystallites formation in the host matrix and hence, on the visible transmission edge of the doped glasses. At the same time, the presence of the semiconductor particles was put in evidence by Raman spectroscopy. The homogeneity of the doped glasses, more precise, the dispersal of the CdS_xSe_{1-x} crystallites in the vitreous matrix was analyzed using a diode laser excitation in the visible range and an adequate device which investigated the relative intensity profile of the emergent beam from the doped glass.

2. Experimental

CdS_xSe_{1-x}-doped aluminophosphate glasses were prepared by a non-conventional wet method. The chemical reagents were: LiOH, $Al(OH)_3$, $BaCO_3$, La_2O_3, H_3PO_4, SiO_2, NaOH, ZnO and as doping elements we used Cd, S, Se. This method provided a better homogeneity of the glass batch and a proposed crystallites' composition of $CdS_{0.5}Se_{0.5}$. After weighing and homogenization of the chemical reagents in a solution of H_3PO_4, gases and water were removed at 100 ^oC for 2h. The preliminary heat treatment initiated the metaphosphates formation even before the beginning of the melting process. The glass was then brought to the melting point (1200 ^oC) and the doping

elements were added under stirring. Casting in preheated moulds and subsequent heat treatment were performed.

In the paper, the doped glasses will be named SDG1 and SDG2 (semiconductor-doped glass with higher basicity due to Na_2O adding).

We aimed at the compositions presented in the Table 1.

Table 1. Oxide composition of semiconductor-doped glasses (SDG).

Oxide	Oxide composition of the SDG1 sample (% wt.)	Oxide composition of the SDG1 sample (% mol.)	Oxide composition of the SDG2 sample (% wt.)	Oxide composition of the SDG2 sample (% mol.)
Li_2O	5.42	20.2	5.27	20.63
Al_2O_3	9.12	10.2	9	10.35
Na_2O	-	-	0.19	0.35
BaO	9.36	7	9.43	7.15
SiO_2	0.36	1.29	0.36	0.7
La_2O_3	3.9	0.7	4	1.41
P_2O_5	71.84	60.61	71.75	59.41
$CdS_{0.5}$ $Se_{0.5}$	1	0.9	1	0.86
ZnO	1	1.5	1	1.4

In the glass composition, we used Na_2O, SiO_2 and ZnO aiming at preventing the volatilization of Cd, S and Se from the melt by forming stable compounds Na_2S, Na_2Se, ZnS, ZnSe, $CdSiO_3$ as shown in [11].

The samples were annealed at 425, 450 and 475 ^oC, for 2h, 4 h and 6 h. Initially, the doped glass is colourless but after the heat treatment, the colour became red or brown indicating the presence of CdS_xSe_{1-x} compounds in the vitreous phosphate matrix as mentioned bellow.

The UV-VIS transmission spectra were obtained with a SPECORD M42 spectrophotometer in the range 400-800 nm.

The Raman spectra were obtained by a Jobyn-Yvon LabRamHR Raman microscope using Ar^+ laser excitation at 514.5 nm, 3mW power and focused to a spot of about 150 μm in diameter.

The SPIRICON LBA 300 device analyzed the 2D and 3D relative intensity profile of the beam coming from the doped glass, when excited using diode laser excitation at 625 nm with a spot diameter of 0.32 mm and a beam power of 12.2 mW.

3. Results and discussion

The purpose of this work was to obtain $CdS_{0.5}Se_{0.5}$ semiconductor molecules as a stable chemical compound in the glass host. The size and the crystalline structure of the semiconductor CdS_xSe_{1-x} were investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) and reported in [12]. The estimated average size of the analyzed semiconductor crystallites was 0.1-0.9 μm. TEM micrographs have pointed out that the SDG1 and SDG2 samples had hexagonal single crystals and hexagonal polycrystalline structure, respectively. We were able to calculate more accurately the lattice parameters of the hexagonal unit cell associated with the polycrystalline diffraction pattern characteristic of SDG2 vitreous matrix, as being: a=4.173 Å and c=6,790 Å [12].

We suggested that the matrix basicity (mixed alkali effect) influences the nucleation and subsequently, the growth of the embedded semiconductor crystallites.

From the CdS_xSe_{1-x} solid solution series and Vegard's law applied for semiconductor band gap, we could estimate that in SDG1 and SDG2 samples, the crystallites' composition, i.e. the x value is 0.42 and 0.55, respectively. SAED patterns estimated that in SDG2 sample, the semiconductor crystallites have a molar percentage of 30 % CdSe that corresponds to $CdS_{0.7}Se_{0.3}$ [12].

Figs. 1 and 2 show the transmission spectra of the SDG1 and SDG2 samples, respectively. Both semiconductor-doped glasses have been annealed at 425, 450 and 475 ^oC for 2, 4 and 6h. Both glass samples exhibit a red shift of the transmission edge with increasing temperature at constant annealing duration and increasing duration at constant temperature. According to our results the sample SDG1 (2h, 425 ^oC) exhibits a transmission edge situated at low wavelength (about 400 nm) as compared with SDG2 sample. One possible explanation would be that at low annealing temperature and short annealing duration the formation of semiconductor crystallites of the same size with increased sulphur content in the doping molecules is favoured and the optical transmission edge appears at low wavelength. At higher annealing temperatures and longer annealing durations the transmission edge is shifted towards higher wavelength due both to the increasing of the selenium content within the CdS_xSe_{1-x} molecules and also to the independent growth of the crystallites nuclei as well as by coalescence. (Eg_{CdS}=2. 45 eV and Eg_{CdSe}=1.74 eV [13]).

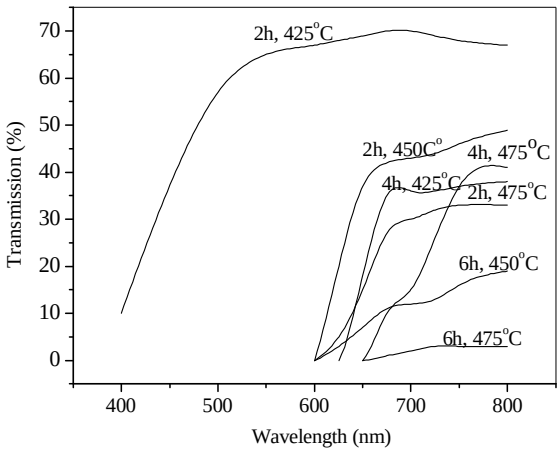


Fig. 1. Transmission spectra of the semiconductor doped glasses belonging to the oxide system Li_2O-P_2O_5-Al_2O_3-BaO-SiO_2-La_2O_3, doped with 1 wt.% $CdS_{0,5}Se_{0,5}$ and 1 wt.% ZnO (SDG1). The glass samples were annealed for 2h, 4h and 6h at 425 °C, 450 °C and 475 °C.

A sharp transmission slope corresponds to a narrow composition range of the crystallites and the transmission slope becomes less sharp at higher annealing duration, which means that crystallites of different compositions are formed during the coalescence process and the vitreous matrix is oversaturated with doping molecules [5].

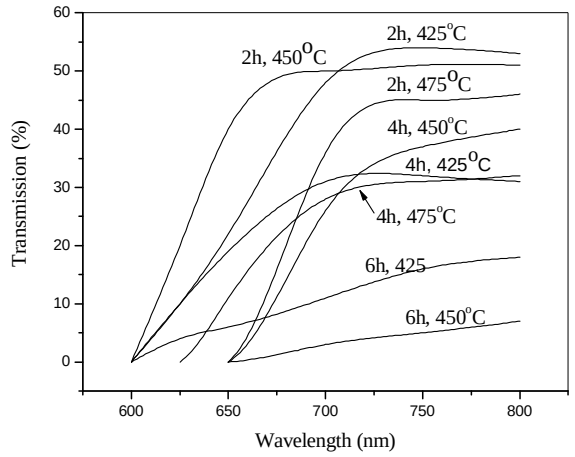


Fig. 2. Transmission spectra of the semiconductor doped glasses belonging to the system Li_2O-Na_2O-P_2O_5-Al_2O_3-BaO-SiO_2-La_2O_3, doped with 1 wt.% $CdS_{0.5}Se_{0.5}$ and 1 wt. % ZnO (SDG2). The glass samples were annealed for 2h, 4h and 6h at 425 °C, 450 °C and 475 °C.

We have to mention that the increasing of the temperature and duration of annealing determine a diminishing of the optical transmission level (see Fig. 2). More and more crystallites are formed, they grow by coalescence (mutual influence) in the bulk glass and they do not allow the visible light to pass, thus the glass colour became dark red or brown.

The difference between the position of the transmission edge for SDG1 (see Fig. 1) and SDG2 (see Fig. 2), annealed at 450 °C for 2 h could be explained by the higher basicity of the SDG2 glass. This last glass sample contains two alkali oxides, Li_2O and Na_2O as network modifiers, interrupting the long chains and providing shorter phosphate chains and phosphate rings. In this case, the mixed alkali effect influences the nucleation and the growing process, forming more bonds with non-bridging oxygen atoms (O^-). These shorter phosphate units could favour the growth of bigger semiconductor molecules changing the composition of the semiconductor crystallites towards higher molar fraction of Se. Consequently, the transmission edge of SDG2 glass annealed at 425 °C for 2 h is shifted towards higher wavelength as compared to SDG1 glass under the same treatment parameters. At higher durations and annealing temperatures, the transmission edges for both glass samples are situated almost within the same range of wavelength.

In Fig. 3, we report Raman spectra for the samples SDG1 and SDG2, annealed for 2 h and 6 h respectively, at 450 °C. The features near 199, 292, 491 and 590 cm^{-1} are Raman lines from $CdS_{0.7}Se_{0.3}$ crystalline compound as indicated for $CdS_{0.7}Se_{0.3}$–doped glasses in [13].

The spectra are in agreement with the reported data [12], corresponding to LO peaks for the binary compounds CdS-like mode [LO(1)] at 292 cm^{-1} and CdSe-like mode [LO(2)] at 199 cm^{-1}. The shoulders on the low-frequency side have been associated with the surface vibrations [13,14].

The lines at higher frequency are combination mode near 491 cm^{-1} [LO(1)+LO(2)] and overtones 2LO(2) at 398 cm^{-1} and 2LO(1) at 590 cm^{-1} [11].

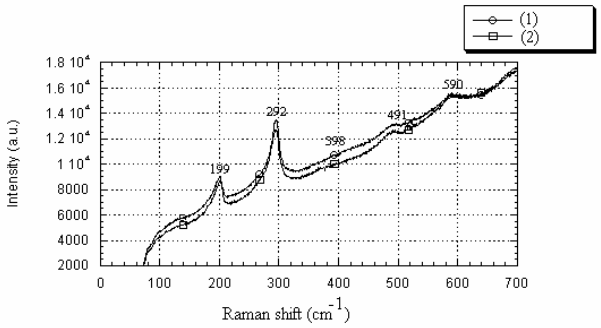
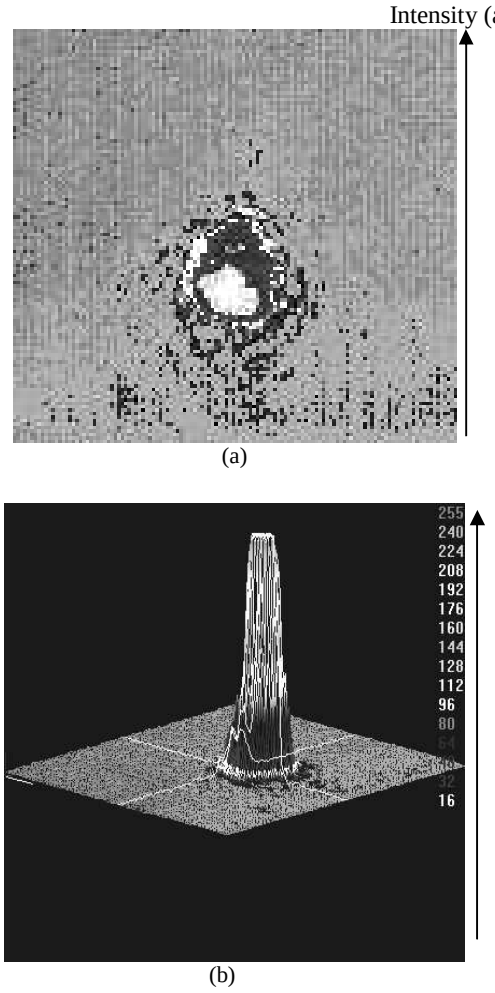


Fig. 3. Raman spectra for SDG1, 2 h annealed (1) and SDG2, 6 h annealed (2), excited at 514.5 nm. The annealing temperature was 450 °C.

Further, we present some information obtained from SDG1 sample, excited by a diode laser at 625 nm. The relative intensity profile was 2D and 3D, analyzed by the SPIRICON LBA 300 devices. Thus, we are able to investigate the homogeneity of the SDG1 sample, actually, the spreading of the CdS_xSe_{1-x} crystallites in the bulk glass. We used a square plate sample, which was irradiated on five square areas (l=5 mm) placed in the middle and in the corners of the analyzed sample (the increment of the spot shift on the sample was 1 mm).

In the Fig. 4 we present some 2D (a) and 3D (b) images of the relative intensity profile obtained by SPIRICON LBA 300 device. The 2D image is a cross-section of the ratio between the intensity of the emergent beam and the intensity of the incoming beam and the 3D image is a three-dimensional profile of the same ratio. In these images, the white colour and black colour denote high relative intensity and low relative intensity sites, respectively.



(a)

(b)

Fig. 4. SPIRICON LBA 300-2D images (a) and 3D images (b) from the SDG1 plate sample, excited by a diode laser at 625 nm.

As we noted above the relative intensity profiles from the respective five areas are quite similar, that demonstrated a uniform spreading of the CdS_xSe_{1-x} crystallites in the host bulk glass.

4. Conclusions

We have shown that the temperature and the duration of the annealing influence the absorption edge of the CdS_xSe_{1-x}-doped glasses, in the visible range. Raman spectra revealed specific features for $CdS_{0.7}Se_{0.3}$ crystallites, which agree with previously reported $CdS_{0.65}Se_{0.35}$ – doped borosilicate glasses. The investigation of the homogeneity of the crystallites carried out by laser excitation has revealed a uniform spreading of the semiconductor chalcogenide particles in the bulk glass.

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