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INFLUENCE OF PROCESSING CONDITIONS ON THE OPTICAL BAND GAP IN THERMO-MECHANICALLY DOPED AMORPHOUS As_2S_3

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In this paper we present a study of influence of thermo-mechanically implemented rare-earth oxides on the optical band gap width of thesamples with an amorphous arsenic sulfide matrix. The pure bulk arsenic sulfide (As_2S_3) and $(As_2S_3)_{100-x}(Nd_2O_3)_x$ chalcogenide glass samples with concentrations up to $x = 2$ at% of Nd_2O_3 were prepared by the low temperature thermo-mechanical method. We have investigated the influences of the duration of the mechanical treatment and the achieved densification temperature of the starting materials. The recorded diffuse reflection spectra have shown that the optical band gap of the samples decreases with the increase of the duration of mechanical treatment and increases with the rise of dopant concentrations. Additionally, there are certain implications that heating of the materials allows the implementation of the dopant molecules into the basic matrix. Performed analysis enabled the optimization of the temperature range and the minimal necessary duration of mechanical treatment of the constituents for the successful preparation.

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1. Introduction

Due to their properties, chalcogenide glasses are very suitable for different applications in optical systems. As they have high transparency in the near infrared and infrared region of the electromagnetic spectrum, they are good matrices for doping with rare-earth materials[1][2]. The main feature which can be used is that the main transitions in rare earth ions are located in the infrared region of the spectrum, in which chalcogenide glass matrices don't have absorption peaks.

The requierement for the cheap glassy materials obtained by the simple synthesis leads to an idea of combining the low temperature thermal treatment of starting materials with the application of high pressures. Calvez and associates registered a patent based on a new method of synthesis of glasses and glass ceramics which are optically transparent in the infrared region of electromagnetic spectrum. Their method includes a step of amorphization of the starting powder by mechanosynthesis, while the starting powder consists of at least one element which is metal and at least one which is chalcogen. Amorphization enables the formation of amorphous powder, which is followed by hot densification in a mold of suitable shape and dimensions [3].

Turyanitsa and associates managed to obtain optical elements in the form of chalcogenide glass plates. The method was based on thermo-mechanical treatment of starting components. Since optoelectronic systems are based on various components made of amorphous materials, and today are equally good or even better than classic electronic systems, the authors aspired to devise a more suitable method of creating of those components than the conventional ones. The usual techniques for the preparation of the the glassy optical elements involve polishing the samples obtained by synthesis in a vacuum sealed quartz tube. In these authors' method a certain property of amorphous semiconductors was used. It is known that with the increasing temperature their iscosity decreases, which makes possible the shaping of a glass grain heated to a temperature close

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to the softening temperature. In this particular work, grains were compressed into a flat shape between the two plates of silica glass, mica or directly onto an optical fiber [4].

In case that the material is to be formed into optical lenses, it is possible to assemble a mold of a desired shape, and use it for designing the necessary glass sample[5]. A great advantage of amorphous materials is the possibility of designing complex final shapes during the preparation, that is without subsequent additional processing. This is true especially for chalcogenide glasses, since they're used in the shape of lenses in thermal imaging.

2. Experimental

The combination of mechanical and thermal preparation and latter compression in the experiments of Turyanitsa et al. and Calvez et al. inspired the authors of this paper and set a challenge to create and investigate a similar method for the well known material As_2S_3.

The synthesis of the samples investigated in this work was carried out with the thermo-mechanical method. The method is based on the mechanical processing of the previously prepared bulk arsenic-sulfide glass (As_2S_3) and the uniform mixing of that basic matrix and dopant powder of neodymium-oxide (Nd_2O_3), followed by hot densification in the mold provided for that purpose. Since conventional methods aren't suitable for doping of chalcogenide glasses with rare-earth oxides because of too high temperatures and chemical changes of rare-earth oxides which they may cause, preparations in these experiments were carried out through a new low temperature technique.The mixture was mechanically treated in an agate mortar with a pestle with the different durations of the process (1, 10 and $30\ \mathrm{min}$). The samples were prepared with different concentrations of the neodymium-oxide dopant, i.e. as a $(As_2S_3)_{100-x}\ (Nd_2O_3)_x$, with $x = 0, 0.2$, 0.4, 0.5, 0.7 and 2 at% of Nd_2O_3. Powder was then poured into a steel mold, and the mold was placed into a heating cell, which was afterwards vacuumed. After reaching and stabilization of the required temperature, the sample was densified with the hydraulic press ($p \approx 40$ atm per sample) and thus densified and quickly taken out in the air in order to rapidly cool and solidify. The resulting samples had a diameter of about 4 mm and the thickness of $1 - 2$ mm.

The densification temperature was in the beginning chosen to be near the temperature of glass forming of the basic matrix of As_2S_3 ($T_g = 212$ °C [6]). Bellow this temperature the produced samples aren't homogeneus and instead appear to be similar to compressed ceramic. The syntheses were also carried out at different temperatures, up to ~ 235 °C, above which it is possible to create a sample, but it becomes so soft that it deforms itself under its own weight upon the extraction from the mold.

In order to determine the effects of the different durations of the mechanical treatment of the starting materials on the optical band gap of the resulting samples, an analysis was performed on the pure As_2S_3 samples as well as on the samples doped with Nd_2O_3, all prepared from the starting materials ground for either 1, 10 or 30 min.

Polarized light microscopy was used to verify the homogeneity of the samples. Performed analysis has shown that the samples were homogeneus and indeed amorphous. In regular microscopy, especially with higher concentrations of the dopant, there are visible certain black spots which disrupt the otherwise homogeneus structure of the synthesized materials.

The resulting samples were analysed via diffuse reflection spectroscopy. The recordings were carried out in the setting for integrating sphere and the spectra themselves were recorded with the QE65000 detector of *Ocean Optics* company. The used software (*Spectra Suite Spectrometer Operating Software*) enabled the simultanious recording of the dependance of Kubelka-Munk functions on the wavelength of the radiation, so that gathered data could be used for finding the optical band gap of a specific sample.

3. Results and discussion

The analysis of the diffuse reflection spectra was based on the well known Kubelka-Munk reflection theory and the optical band gap itself was determined from the extrapolated dependance of the tranformed Kubelka-Munk function on the energy of the incoming radiation [7][8]:

$$[F(R_\infty)h\nu]^2 = C\left(h\nu - E_g\right) \tag{1}$$

In equation (1), $F(R_\infty)$ is the Kubelka-Munk function, R_∞ stands for the reflection of the thick enough sample, $h\nu$ is the energy of the incoming radiation and E_g is the value of the optical band gap. C represents the constant of proportionality. Example of the extrapolations of linear parts of tranformed Kubelka-Munk curves is presented in Figure 1. The shown examples represent the four arsenic-sulfide samples from Table 1. The scattering of some data points which is visible in the range of greater energies is due to the multiplication of the values from some data sets, so they could be all seen in the same graph.

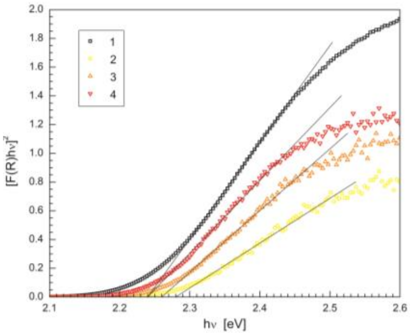

Fig. 1.The curves of dependence of $[F(R_\infty)h\nu]^2$ on $h\nu$ of the bulk and the three prepared As_2S_3 samples. The numbers match with the serial numbers of materials in the Table 1.

All the results describing the effect of mechanical treatment on the optical band gap are summarized in Table 1 and Fig. 2. The numbers next to the data points in the graph correspond to the serial numbers of the materials in the Table 1. The dashed lines are auxiliary, while the solid black line marks the optical band gap energy of the used bulk arsenic-sulfide. The collected data shows that the optical band gap width of the samples decreases with the increase of the duration of mechanical treatment. This could be the consequense of the improved bonding of the smaller particles into the final samples.

Since it can be noticed in the Fig. 2. that the 30 min of mechanical treatment of pure As_2S_3 enables preparation of the sample with the same width of the optical band gap as the bulk, it was concluded that that time of processing is minimal for this method of preparation.

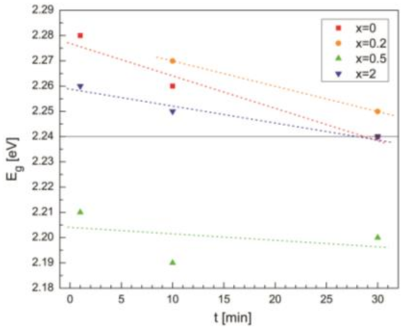

Fig. 2.The dependence of the values of the optical band gap of the studied samples on the duration of the mechanical treatment of the starting materials.

Table 1. Values of the energy of the optical band gap, temperatures of densification and durations of mechanical treatment for the specified samples.

No.	Material	T [°C]	t[min]	E_g[eV]
1	As_2S_3	215	bulk	2.240(1)
2			1	2.280(2)
3			10	2.260(1)
4			30	2.240(1)
5	$(As_2S_3)_{99.8}(Nd_2O_3)_{0.2}$	213	10	2.270(2)
6			30	2.250(1)
7	$(As_2S_3)_{99.5}(Nd_2O_3)_{0.5}$	230	1	2.210(2)
8			10	2.190(1)
9			30	2.200(2)
10	$(As_2S_3)_{98}(Nd_2O_3)_2$	234	1	2.260(1)
11			10	2.250(1)
12			30	2.240(1)

Therefore, in further analysis in this paper, only such samples were taken in consideration. Of course, the use of more advanced equipment such as planetary mills will surely give significantly different results, which is why it is considered for future research. However, the use of such equipment would require larger amounts of the starting components, since the removing of the ground powder from the steel balls would otherwise present a problem.

Fig. 3 shows the comparative view of the reflection spectra of the three $(As_2S_3)_{98}(Nd_2O_3)_2$ samples, one of which was pressed unheated and the other two heated up to 234 °C and then densified. One of the heated samples was ground for 1 min, while others were mechanically treated for 30 min. It can be noticed that the absorption peaks of the $Nd_2O_3$are much more pronounced in the spectrum of the unheated sample. It can be concluded that the dopant didn't react with the basic matrix because the applied method of the mechanical treatment simply wasn't adequate for chemical bonding of neodymium-oxide with the glass. However, after heating and densification, the absorption peaks significantly decrease. This indicates that the part of Nd_2O_3 possibly does get implemented into the As_2S_3 matrix, but in such a way that it changes it's structure. Also, the intensities of the absorption peaks in the two heated samples seem to be very similar, therefore the supposed chemical change in the samples is indeed the consequence of the heated densification rather than the mechanical treatment. Manual grinding doesn't seem to provide enough force for the microscopic grains of Nd_2O_3 to break appart into smaller pieces, which could perhaps explain the previously mentioned black spots in higher concentration samples.

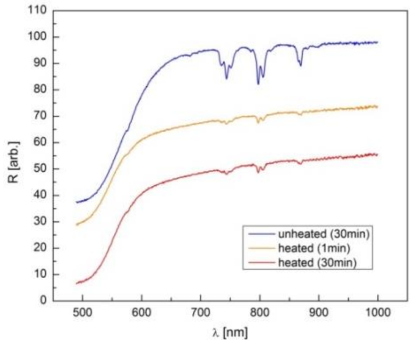

Fig. 3.The reflection spectra of the samples of $(As_2S_3)_{98}(Nd_2O_3)_2$, one of which was ground for 30 min and then pressed unheated, and the other two for 1 min and 30 min, and then pressed after heating up to 234 °C.

For analysing the effects the different concentrations have on the optical band gap of the final samples, the values of energy of the optical band gap of the samples, their dopant concentrations and temperatures of densification are presented in Table 2. and the observed dependances are shown in Figure 4.

Table 2.Values of the energy of the optical band gap, temperatures of densification and concentrations of dopants for the specified samples. All of the samples were ground for $30\ min$.

No.	Material	T [℃]	E_g [eV]
1	$\mathrm{As_2S_3}$	215	2.240(1)
2	$\mathrm{As_2S_3}$	230	2.206(6)
3	$\mathrm{(As_2S_3)_{99.8}(Nd_2O_3)_{0.2}}$	216	2.280(2)
4	$\mathrm{(As_2S_3)_{99.6}(Nd_2O_3)_{0.4}}$	214	2.300(3)
5	$\mathrm{(As_2S_3)_{99.5}(Nd_2O_3)_{0.5}}$	230	2.190(2)
6	$\mathrm{(As_2S_3)_{99.3}(Nd_2O_3)_{0.7}}$	225	2.170(2)
7	$\mathrm{(As_2S_3)_{98}(Nd_2O_3)_2}$	234	2.250(1)

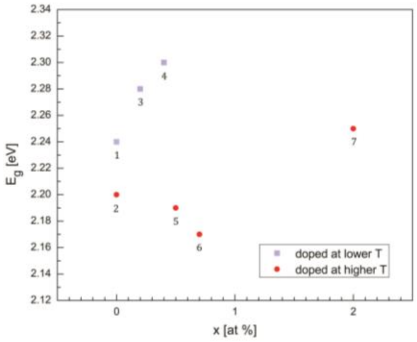

Fig. 4.The dependence of the values of the optical band gap of the observed samples on the concentrations of dopants for the samples doped with Nd_2O_3 *and the samples of* As_2S_3*. The numbers next to dots in the graph match the serial numbers of materials in the Table 2.*

It can be concluded that the rise of the dopant concentration causes the increase of the values of the optical band gap for the samples with similar temperatures of densification. Since the results indicate that the increase is continual, it can be presumed that the dopant is successfully integrated into the basic matrix. The possible explanation is that the addition of the dopant changes the structure of a glassy semiconductor in such a way that the component atoms distance themselves further away from each other and so the optical band gap increases. J. Tauc et al. [9] calculated the position of absorption edge for amorphous arsenic-sulfide and so the width of the optical band gap is $2.35 - 2.38$ eV. These values are slightly higher than those presented in our paper (Table 2.), but this could be the consequence of the fact that the reffered authors used conventional methods of synthesis of chalcogenide glasses. However, various techniques of deposition of the As_2S_3 thin films provide samples with the values of the optical band gap ranging from 1.82 eV to 2.38 eV [10], which is in accordance with the results in our paper. The comparison of the two groups of data points (blue for lower and red for higher temperatures) implies that in the general case the higher temperatures of densification of the material induce the lower values of energy of the optical band gap. Higher temperature enables better bonding of the added components in the material, which is a possible explanation of the observed effect. Each of those lines stands for a distinct temperature range, inside which the dependance of E_g appears to be linear. In other words, the dependence of the optical band gap width on the dopant concentration of the samples densified at lower temperatures doesn't intersect with the dependence of the samples pressed at higher temperatures.

4. Conclusions

The combination of thermal and mechanical treatment of the components in the process of preparation of the samples proved to be successful, both with just a basic matrix of As_2S_3 and doped with Nd_2O_3. Diffuse reflection spectra were recorded and analysed for the purpose of studying the change of the optical band gap and divising a low temperature method of synthesis of chalcogenide glasses doped with rare-earth oxides. Prepared semiconducting materials had slightly different homogeneity than the bulk, but in the optical properties they were very similar to it.

Temperature study has shown that the heating of the starting materials is necessary for the successful preparation, but it also shows possible alterations of the dopant structure. Also, for fixed concentration of dopants the increase of maximal temperature of densification causes the decrease of the optical band gap. However, within a certain temperature range, the rise of the dopant concentration increases the width of the optical band gap. Based on the results, there are indications that the dopant is integrated into the arsenic sulfide matrix.

Acknowledgments

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