Influence of Fe on microhardness and dissolution rate of SbSI chalcogenide glass matrix

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This paper presents the investigation of chemical stability and microhardness of ferroelectric glasses Sb-S-I doped with iron. We have investigated the influence of iron atoms introduced into the glass matrix, as well as other factors causing the change of chemical stability. The temperature measurements allowed us to determine the activation energies that define the solubility rate on the certain temperature. Increasing the doping level of iron atoms appears to decrease the chemical stability of the system. The mechanical measurements showed that the iron atoms increase Vickers microhardness of the system confirming their important role in the reinforcing the glass matrix.

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1. Introduction

Chalcogenide glasses are semiconducting materials containing chalcogenide elements, i. e. sulphur, selenium and tellurium. They possess unique properties being very attractive for the research and different applications [1–3]. Mainly due to their optical non-linearity and transparency from visible to infrared radiation, they find various applications in infrared cameras, diffractive, waveguide and fiber structures [4,5].

It has been shown that small variations in their composition, for example alloying them with transition metal atoms, can significantly change almost all their physical properties. Doping of three-component ferroelectric glass-ceramics Sb-S-I with iron atoms appears to be very interesting due to the possibility of tuning electrical, magnetic and mechanical properties with the concentration of dopant atoms [6].

Chemical stability, which tells about material's resistance to different chemicals that may change its original properties, is very important for chalcogenide glasses. Previous investigations have shown that chalcogenides generally have excellent chemical durability in normal atmospheric conditions being quite stable in acidic solutions, but less stable in diluted bases and some solvents containing amino groups [1,7,8]. Even the lower stability in some chemicals could be beneficial for certain reasons such as the rougher surface formation, surface preparation for metallographic examination, enhancement of the optical contrast of amorphous films in the amplitude-phase storage of optical information, etc.

Beside the chemical stability, mechanical properties of chalcogenide glasses play very important role for their practical applications [9,10]. Due to the high brittleness of these materials, it is essential to investigate their resistance to surface damage caused by the sharp mechanical contacts [11]. Indentation microhardness measurements are frequently used for the investigations of mechanical properties of these materials. They enable simultaneous determination of several mechanical quantities from the indentation curve, which are important for the practical applications and establishment of correlation with the structural elements.

The present study reports on the investigations of the chemical stability in KOH solution and mechanical properties of chalcogenide glasses from $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{100-x}$ system. The part of results referring to chemical stability investigations were reported earlier [12]. The measurements of the mechanical properties were performed using an instrumented indentation method with an emphasis on the Vickers microhardness. As an aid to better understanding of these parameters, we also investigate the other factors, such as the glass composition and its correlation with the investigated behavior of the material.

2. Experimental

The semiconductive chalcogenide glasses from the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{100-x}$ system were synthesized from high-purity elements (99.999%) by the method of cascade heating. It is worth mentioning that the maximum doping concentration was 5 at% of iron, because it was previously showed that for the higher concentration system crystallizes. The synthesis of the glasses was described in detail earlier [13].

The influence of basic solution on the samples was investigated for x = 0.01, 0.1, 0.8, 1.5, 3, 5 at% iron concentration. Measurements were performed in several steps. Prior to the measurements, the samples were mechanically polished with abrasive powder of different grain sizes to obtain regular geometric shapes (cuboid, cube) with the thicknesses of few mm, which allow easier

and more accurate determination of the area of samples. After that, the initial masses and the dimensions of the samples were measured and then they were treated in KOH solutions with concentrations of 0.5 mol/dm^3 and 1 mol/dm^3 and different temperatures in a range from 273-333 K. The chemical reaction was stopped every 20 s by sinking the samples into distilled water. Then, the samples were dried and their masses and dimensions were measured again. This procedure was repeated ten times for each sample.

The dissolution of chalcogenides in a solvent can be described by heterogeneous reaction, which includes several stages: transport of the reacting particles to the reacting surface, surface chemical reaction and removal of the products from the reaction zone [14]. Chemical stability of the system is determined by the rate of the heterogeneous chemical reaction on the sample surface, namely solubility rate. The solubility rate in a chemical reagent at various concentrations was determined by an indirect method via weight loss, using the following equation:

$$\omega = \frac{\Delta m}{SM\Delta t} \quad (1)$$

where Δm is the mass change during the dissolution time Δt, S is the area of the sample and M is the molecular mass of the conditional chemical unit.

The mechanical properties were investigated on chosen representative bulk samples for x = 0.01, 0.8, 1, 1.5, 2, 3 at%. Prior to the measurements the samples were embedded into the polyester resin and polished with abrasive powders of the appropriate grain size (260–28 μm) to a mirror shine. Measurements were carried out on Fischerscope HM2000 S system device with Vickers diamond indenter, calibrated according to the DIN EN ISO 14577-3 standard using a BK7 type reference block. The samples were exposed to different loads in a range from 20-600 mN, while the load change rate during the cycle was 1 N/s.

3. Results and discussion

Since it was reported that the stirring of the solution has almost no influence on the dissolution rate of chalcogenide glasses, it can be considered that the dissolving of the investigated samples was the result of the chemical reaction on the sample's surface [1,8,15]. This assumption makes possible the calculation of the solubility rate using equation 1, where the change of the areas and masses of the samples in a certain periods of time are experimentally determined. The color of the basic solution was monitored during the measurements and it stayed unchanged.

The dependence of the dissolution rate on time at 303K for the solutions with concentrations of 0.5 and 1 mol/dm^3 respectively is shown in Fig. 1 a and b. In both cases the dissolution rate exponentially decreases with the sample treatment time, which is in agreement with previously obtained results for chalcogenide glasses although their chemical stability is slightly higher when compared to other similar systems [7,8]. As expected, the dissolution rate increases for the higher concentration of the basic solution.

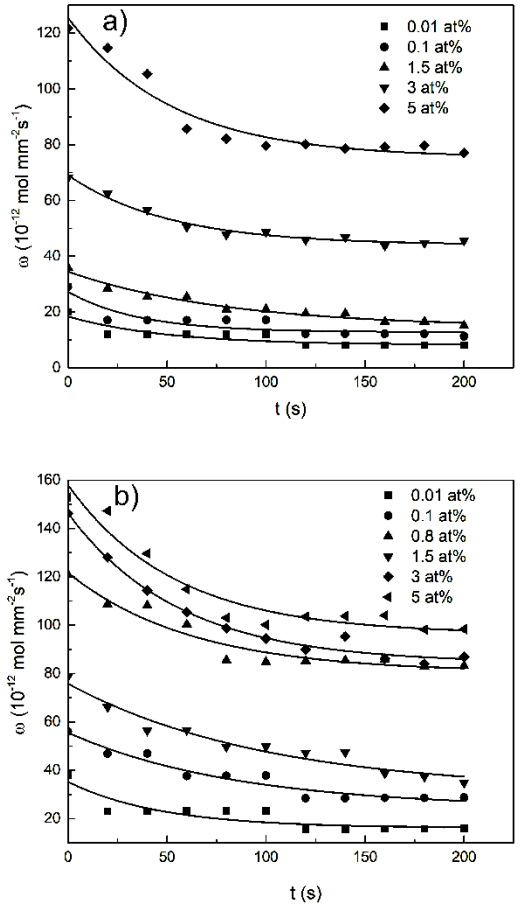

Fig. 1. The dependence of the solubility rate on time at 303 K for the solutions with concentrations of a) 0.5 mol/dm^{3}and 1 mol/dm^3

Fig. 2 shows the dependence of solubility rate on iron content at t = 100 s and 303 K for the solution with concentration of 1 mol/dm^3. The solubility rate increases up to 0.8 at% of iron, which is followed by its decrease up to 1.5 at % and its repeated increase. The similar behavior was found for the glass transition temperature which increases with the increase of iron content up to 0.8 at % and further decreases with its increase. The optical band gap showed opposite trend in the behavior decreasing up to 0.8 at % and further increasing, while the specific conductivity also showed the change in the behavior about the same Fe concentration. These sudden changes at 0.8 at% indicate significant changes in the glass network when iron content is above 0.8 at%, such as the presence of isolated iron centers at these concentrations [6,13,16].The increase of iron content in Sb-S-I matrix decreases the chemical stability of the system indicating catalytic role of iron atoms in chemical dissolution.

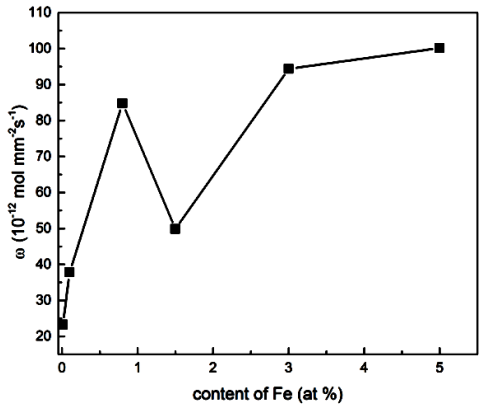

Fig. 2. The dependence of the solubility rate on Fe content at 303 K at 100 s for the solution of 1 mol/dm^3

The strong influence of iron content on the chemical stability can be explained by the fact that the changes in the glass composition cause the changes in the content of some structural units in the glass matrix. Larger amount of iron atoms in the glass matrix is associated with the appearance of deficit of sulphur content, especially on higher concentrations, leading to the emergence of new non-stoichiometric structural elements. The iron atoms do not build in actively into the network but are randomly distributed in the glass in the form of sulfides and homopolar bonds. This non-stoichiometric distribution of structural units might lead to the lower chemical stability of the overall system and thus the increase of the solubility rate with the increase of iron content.

From the measurements on different temperatures, it can be observed that the solubility rate increases with the temperature of the solution but not as fast as with the increase of iron content. This is summarized in Fig. 3.

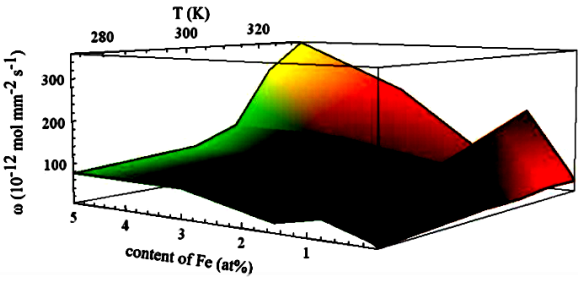

Fig. 3. The influence of temperature and Fe content on the solubility rate for the solution of 1 mol/dm^3

The temperature measurements enabled determination of the activation energies for the dissolution from the slope of the logarithmic plot of ω with 1/*T* as shown in Fig. 4 a. The calculated values for the solution of 1 mol/dm^3 are represented in Fig. 4 b. The activation energy increases with the increase of iron content up to 0.8 at%. The increase of iron content up to 1.5 at% results in the decrease of this parameter but further increase leads to the repeated increase of the activation energy from 3 at%. This is again in correlation with the non-monotonic behavior of other physical properties about the concentration of iron atoms of 0.8 at%.

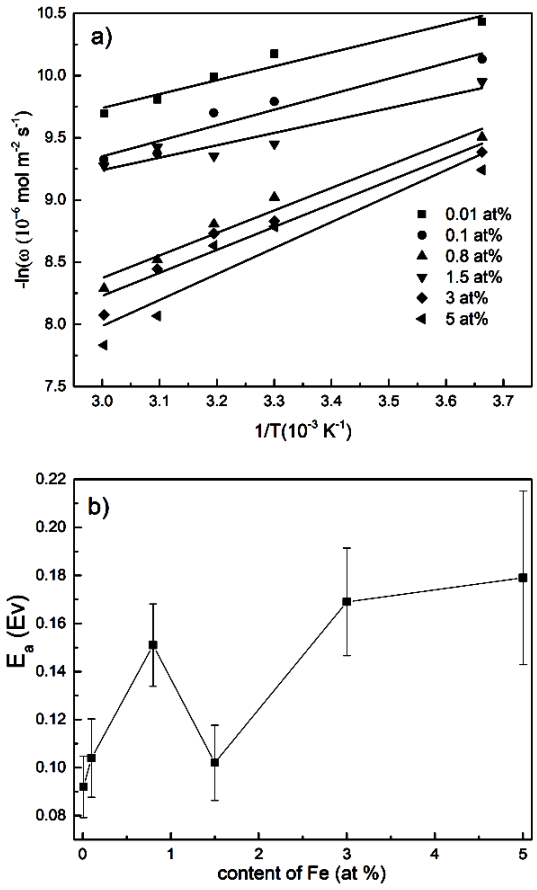

Fig. 4. (a) Dependence of Inω on 1/T (b)The influence of Fe content on the activation energy for the solubility rate for the solution of 1 mol/dm^3

The load-displacement curves obtained from measurements of mechanical characteristics for the sample with 3 at% of Fe during three cycles of loading and unloading are shown in Fig. 5 as representative for all investigated samples. The overlapping of the curves from all three measurements indicates a high level of reproducibility. The dependence of Vickers microhardness on the applied load is represented in Fig. 6.

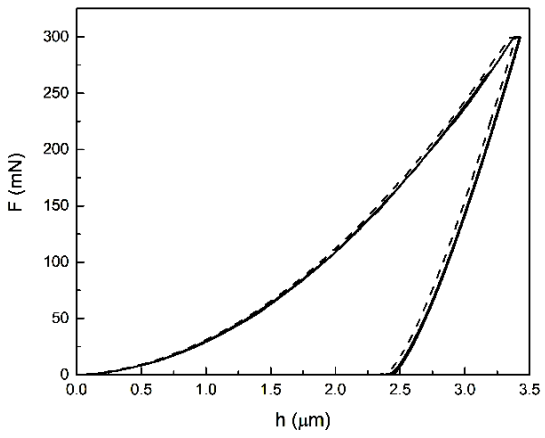

Fig. 5. Typical load–displacement curves, obtained for the samples with 3 at.% Fe, with maximum loading force of 300 mN

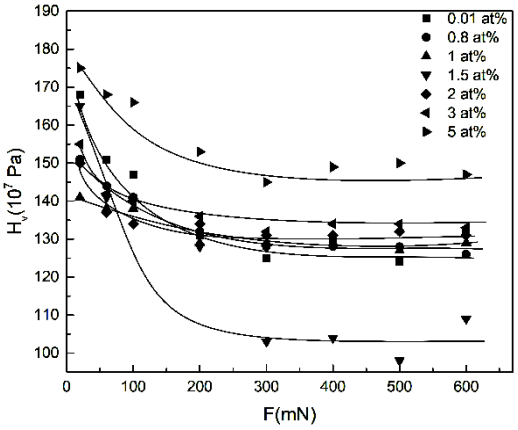

Fig. 6. Vickers hardness versus the applied test force for glassy samples with different iron content

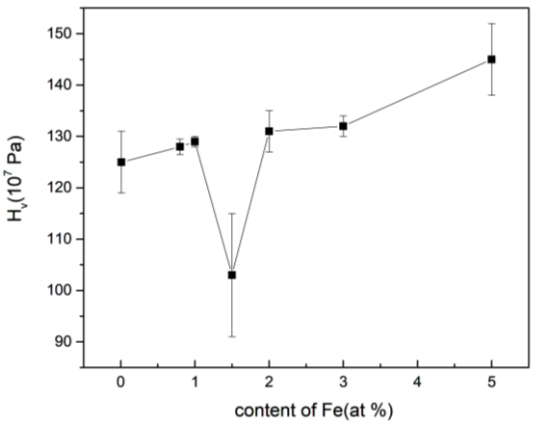

Fig. 7. Dependence on Vickers microhardness on Fe content for maximum loading force of 300 mN

The decrease of the Vickers microhardness with the increase of the applied force in the force range of 20–300 mN, after which it becomes constant occurs for all investigated compositions and is in agreement with the normal indentation size effect [17,18]. The obtained H_v values in the range (98-175)·10^7 Pa are comparable to those obtained in our previous investigations for other chalcogenide glasses [19,20].

To examine the influence of the composition on the microhardness, we have chosen the microhardness values obtained for the load of 300 mN as a point where it becomes approximately constant. The results are presented in Fig. 7. The measurements on the samples with different Fe concentrations revealed that the microhardness increases up to 1 at% Fe followed by its drop up to 1.5 at% and repeated increase for higher Fe concentrations (Fig. 7). If compared with Fig. 1, one can notice very similar dependence of the dissolution rate and Vickers microhardness on Fe content, which is not unexpected due to the fact that this system changes its behavior about this Fe concentration for previously mentioned physical parameters. The increase of the microhardness with the increase of Fe content, except for the sample with 1.5 at % Fe, indicates that the introduction of iron atoms into Sb-S-I matrix changes the share of some structural units and consequently overall bond strength of the system. In other words, the introduction of Fe atoms increases the solidity and rigidity of glass network. On the other hand, the fact that the chemical stability decreases with the increase of Fe content can be explained by the formation of homopolar bonds which take the dominant part in the dissolution, while the other bonds which actually reinforce the matrix do not take part in this process.

4. Conclusions

In this paper we have demonstrated that doping the chalcogenide glasses from Sb-S-I system with iron atoms decreases the chemical stability of the system in KOH solution, which was determined by the rate of the heterogeneous chemical reaction on the sample surface. The calculated values of the dissolution rate show that the chemical stability of this system is slightly higher when compared to other similar systems. As expected, the chemical stability decreases with the increase of KOH solution concentration and temperature. The measurements of Vickers microhardness showed that it increases with the iron content and that their introduction reinforces the glass matrix. The Vickers microhardness showed a pronounced normal ISE in the range of lower loads. All measured and calculated parameters related to the chemical stability and microhardness experience the change in the behavior about 0.8-1 at% of iron, which is in good agreement with other measured physical properties for this system, indicating significant changes in the glass network at that iron concentration.

Acknowledgments

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