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Are the Temperature Sensors Based on Chalcogenide Glass Possible?

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Abstract. Principal possibility of the using of chalcogenide glasses (on the example of $Ge_{18}As_{18}Se_{64}$) as active media for temperature sensors is considered in this work. Differential scanning calorimetry testing of the investigated glasses showed that 2 years of natural storage does not lead to the drift of their parameters (glass transition temperature and endothermic peak area). Investigations of the temperature dependence of optical transmission spectra showed the linear character of optical band-gap changes with a temperature. Temperature sensitivity index for glassy $Ge_{18}As_{18}Se_{64}$ was estimated to be equal to the $\sim 1.2 \cdot 10^{-3}$ eV/°C.

Introduction

Nowadays, chalcogenide glasses (ChG) as typical representatives of network glasses have found their wide applications in modern sensorics, optoelectronics, photonics, telecommunications, acoustooptics, xerography, lithography, etc [1]. In particular, they acquire numerous potential applications in civil, medical and military areas, including chemical sensing, laser power delivery, imaging, scanning near field microscopy/spectroscopy, fiber IR sources/lasers, optical amplifiers/switches, etc [2].

In this paper we report on the possibility of ChG application as active media for temperature sensors. Our investigations are based on the fact of quasi-linear dependence of the ChG optical band-gap width on ambient temperature [3,4]. It is known that temperature response of fundamental optical absorption edge position for these materials being close to 100 pm/°C within a wide temperature range up to the glass transition temperature T_g [3,4]. In addition to the excellent environmental stability (humidity insensitivity), low production costs, simple molding and high-reliable fiber-drawing routes, it can put ChG in a strong concurrence to known analogues on the worldwide sensors market.

All investigations were performed on the example of $Ge_{18}As_{18}Se_{64}$ ChG as typical covalent network glass. As a rigid glass [5], $Ge_{18}As_{18}Se_{64}$ ChG should be resistant to the physical ageing processes proper to disordered materials [6]. However, experimentally obtained by temperature-modulated differential scanning calorimetry (DSC) method ranges of floppy, self-adaptive and rigid phases in some binary ChG systems [7,8] were corrected within conventional DSC [9,10]. Under such conditions we forced to verify experimentally the ability of glassy $Ge_{18}As_{18}Se_{64}$ to physical ageing.

Experimental

$Ge_{18}As_{18}Se_{64}$ ChG samples were prepared by conventional melt-quench method from a mixture of the high-purity elemental germanium, elemental selenium and As_2Se_3 glass in evacuated quartz ampoule (~10^{-6} Torr). The sealed ampoule containing ~10 g of the raw ingredients was gradually heated (2 °C/min) up to 950 °C in a rocking furnace and rocked during 48 h at this temperature in order to make the melt homogenous. The melt was quenched within the regime of the switched off furnace and cooled down to the room temperature in about 14 hours. Obtained bulk samples were cut on the plane-parallel plates and polished up to the optical quality.

Testing of the physical ageing ability of ChG was performed by DSC as the most informative experimental method for such investigations [9,10]. The samples were measured using NETZSCH 404/3/F microcalorimeter after two years of natural storage. Then samples were subjected to a rejuvenation procedure, which included heating of the samples to ~50 °C above of the glass transition temperature, equilibrating of the obtained supercooled liquid and further its cooling to the room temperature. In such a way, it is possible to achieve glassy state close to the initial as-prepared one [11].

The DSC curves were recorded in the ambient atmosphere with q = 5 °C/min heating rate. Three independent DSC measurements with samples of close masses were performed to confirm the reproducibility of the results. Glass transition temperature T_g was determined from DSC heating data as cross-point of tangents at the beginning of glass-to-supercooled liquid transition (a so-called "onset" T_g value) using Proteus® software. Proteus® was also used for the determination of endothermic peak area A in the vicinity of glass transition. Statistical deviation of T_g for different samples of same prehistory did not exceed ± 0.3 °C, while the error for peak area determination was about 2 %.

Optical transmission spectra of the $Ge_{18}As_{18}Se_{64}$ ChG were recorded in the fundamental optical absorption edge region using AvaSpec-2048 spectrometer (*Avantes*, Netherlands). The air-flow heating and cooling of samples were provided in specially constructed temperature chamber with accuracy of ± 0.5 °C. The temperature was changed linearly with a 5 °C/min rate and transmission spectra were recorded through each 10 °C. Investigations were performed in *in-situ* regime (samples remained in the same place of the temperature chamber during the whole experiment). Optical band-gap width E_g was chosen as a numerical parameter for estimation of observed temperature-induced effects. This parameter was calculated using Parav-V2.0 computer program with accuracy of ± 0.005 eV [12].

Results and discussion

DSC curves of the 2-years aged and rejuvenated $Ge_{18}As_{18}Se_{64}$ ChG are shown on the Fig. 1. T_g and A values of rejuvenated ChG equal to 233.8 °C and 1.1 J/g, respectively. The same DSC-parameters of 2-years aged ChG are 233.0 °C and 1.5 J/g, respectively. So, 2 years of natural storage of the samples led to the decrease of T_g by 0.8 °C, while A increased by 0.4 J/g. Taking into consideration the accuracy of DSC-parameters determination, we can conclude that such changes are negligible and 2 years of natural storage does not lead to the essential ageing of $Ge_{18}As_{18}Se_{64}$ ChG.

The temperature behavior of the optical transmission of glassy $Ge_{18}As_{18}Se_{64}$ in its fundamental optical absorption edge region was investigated in the range from the room temperature up to the end of glass transition region. Some of the experimentally obtained optical transmission spectra of $Ge_{18}As_{18}Se_{64}$ ChG are shown on the Fig. 2. As it obvious, position of the fundamental optical absorption edge strongly depends on the temperature: increase of the temperature leads to the long-wave shift of transmission spectrum.

Temperature dependence of the E_g and DSC curve of rejuvenated $Ge_{18}As_{18}Se_{64}$ ChG are shown on the Fig. 3. E_g exhibits linear dependence on the temperature below glass transition region. Such behavior fully correlates with known data of the quasi-linear temperature behavior of the E_g for other ChG systems [3,4]. Temperature dependence of E_g within the glass transition region deviates from the linear behavior. The same effects were found in the case of the temperature dependence of mechanical properties of $Ge_{22}As_{20}Se_{58}$ ChG [13]. Since linear (or quasi-linear) temperature dependence of some physical parameter is required for temperature sensing, so the operation range of feasible $Ge_{18}As_{18}Se_{64}$-based temperature sensor should be limited by $t_{max} \approx 200$ °C.

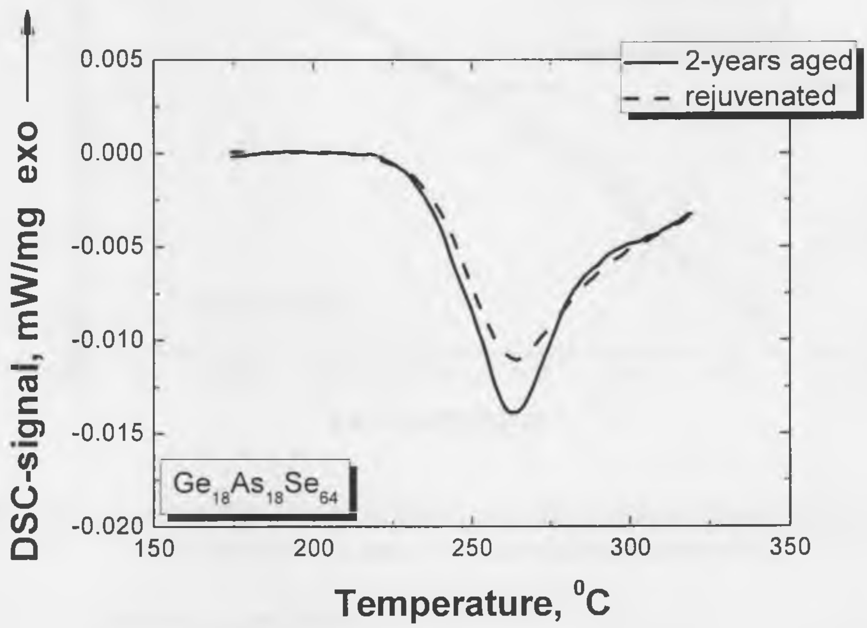

Fig. 1. DSC curves of the 2-years aged (solid curve) and rejuvenated (dash curve) $Ge_{18}As_{18}Se_{64}$ ChG.

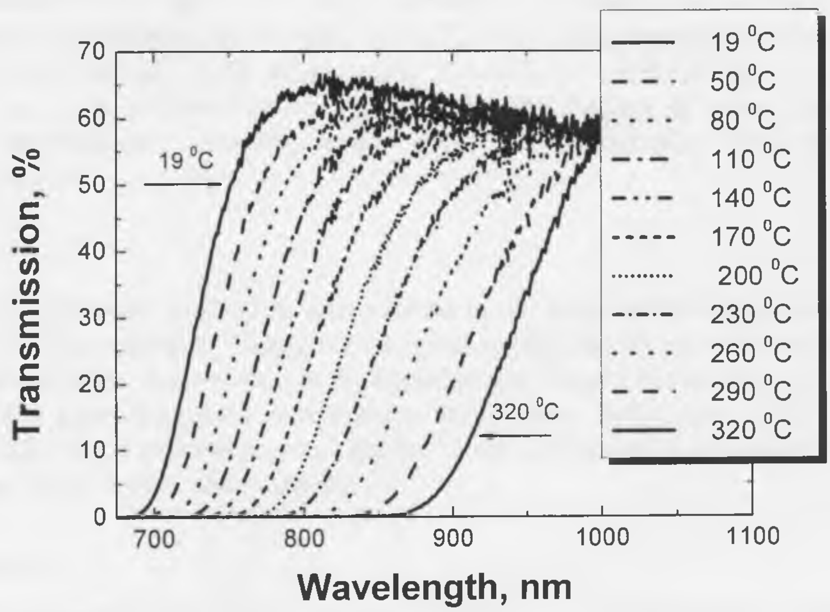

Fig. 2. Optical transmission spectra of $Ge_{18}As_{18}Se_{64}$ ChG at the different temperatures.

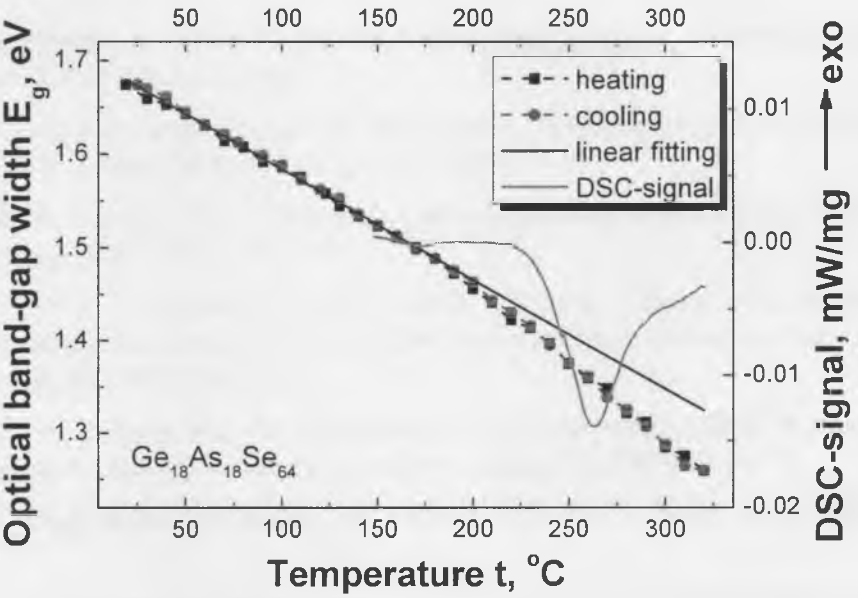

Fig. 3. Temperature dependence of the E_g and DSC-signal of $Ge_{18}As_{18}Se_{64}$ ChG. Yellow box corresponds to the non-linear range of E_g.

One of the most important characteristics of the sensors is sensitivity to the measured parameter. In our case the temperature sensitivity index β corresponds to the slope of the straight line approximating linear range of E_g on the Fig. 3. In other words, β is change in a value of E_g due to the changing of the temperature by 1 °C. Temperature sensitivity index β for $Ge_{18}As_{18}Se_{64}$ ChG equals to the ~1.2 meV/°C while the average deviations of experimentally obtained E_g points from the averaged straight line (Fig. 3) – to the ~2.3 meV/°C. It means that accuracy of the feasible $Ge_{18}As_{18}Se_{64}$-based temperature sensor can be ± 2 °C. But taking into account the accuracy of the E_g determination (± 0.005 eV), this characteristic increases to ± 4 °C being too large for precise device application. This problem can be resolved by the finding of more precise way of E_g determination. Nevertheless, obtained results show that principally ChG can be used for temperature sensing.

Conclusions

Possibility of the application of ChG as active media in the temperature sensors was tested by way of glassy $Ge_{18}As_{18}Se_{64}$ example. Negligible physical ageing ability was shown to be proper for these glasses. Temperature dependence of E_g demonstrates linear behavior in the range from room temperature to the glass transition temperature while some deviations from the linearity are observed within the glass transition region. Obtained results indicate the possibility of application of ChG as active media for temperature sensors.

Acknowledgments

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