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THERMAL ANALYSIS OF SULFIDE Ge–Ga GLASSES DOPED BY PRASEODYMIUM

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Abstract

The present study shows the dependence of the temperature of glass transition – T_g upon the presence and quantity of doping Pr atoms. Substantial effect of the form – chemical nature of compound from which the doping atoms are incorporated into the glass has been displayed as well. With the increase of the content of sulfidic form T_g values approach the level of undoped glasses. Thus, if the studied glasses are doped by sulfidic form, bonded are as atoms of Pr so atoms of S. Glasses doped by halogenous source of Pr behave differently; the shift of the T_g value does not change with the amount of the dopand, displaying the anion deficiency of glass stoichiometry in studied interval of halogenous dopands. Generally, a very slight non-stability of the glass against the oxidation in temperature region of glass transition is observed.

Keywords: glass transition, Pr dopand, sulfide Ge–Ga glasses, T_g values

Introduction

There is a growing interest in the new family of special glasses involving fluoride, chalcogenide and heavy metal glasses. The research and application interests [1–5] are extended due to the properties of those glasses covering transmission in middle and far infrared region of spectra, lower values of phonon energies and higher values of refraction indexes opposite to silica glasses. Quantum efficiency of luminescence depends on both chemical and physical purity and the solubility of ions of rare earth [4]. Thus, from the point of view of routine production, it is necessary that the monoliths exert reproducible properties.

Sulfide Ge–Ga glasses have the largest rare earth solubility, more than 2 mass% [6]. Sulfide Ge–Ga glasses with basic composition of $Ge_{25}Ga_{10}S_{65}$ and those doped by praseodymium (Pr) represent technologically interesting group of glasses for the above mentioned areas of optics and optoelectronics [1–4, 6]. The fibres themselves are produced by pulling up the monoliths at elevated temperatures and, moreover, the

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original monoliths are synthesized of powders with the corresponding composition in a variety of regimes of thermal treatment. Thus, the knowledge of the physical properties, and their changes in the process of thermal treatment [6] is crucial for the control of technological aspects of fibres preparation An earlier study [3] showed the dependence of electrical properties of this group of glasses upon the composition of raw materials, chemical composition of admixtures as well as matrix material.

The aim of this present work has been to study the thermoanalytical characteristics of doped $Ge_{25}Ga_{10}S_{65}$ glasses. The doping atoms of Pr have been introduced into the glasses *in situ* during the primary synthesis in the concentration of 500–6000 ppm. Simultaneous TG-DTA methods of thermal analysis have been successfully used.

Experimental

Samples of glasses have been synthesized by the method invented in the Institute of Inorganic Chemistry Academy of Sciences of Czech Republic, the details can be found elsewhere [1, 4]. The following compositions have been the subject of the present study: $Ge_{25}Ga_{10}S_{65}$, $Ge_{25}Ga_{10}S_{65}$ with 500 ppm Pr in sulfide form, $Ge_{25}Ga_{10}S_{65}$ with 3000 ppm Pr in sulfide form, $Ge_{25}Ga_{10}S_{65}$ with 6000 ppm Pr in sulfide form, $Ge_{25}Ga_{10}S_{65}$ with 1000 ppm Pr in halide form, $Ge_{25}Ga_{10}S_{65}$ with 3000 ppm Pr in halide form.

TG and DTA curves have been simultaneously measured by the device SDT 2960 T. A. Instruments in Pt crucibles in air. The other conditions of thermal measurements have been as follows: mass sample 20 mg, temperature increase 5°C min^{-1}, temperature range from 20 to 550°C. The use of the series of TA 3100 analytical programs gave the characteristics of thermal stability of glasses: Δm values, DTA maxima and, finally, glass transition defined by T_g values. The reproducibility of the results has been confirmed by the repeated measurements. Glass transition, as the kinetic effect that occurs at the transition from supercooled liquid to a glassy solid state, can be characterised by various quantities, where the most frequent is the glass transition temperature, T_g. Any method of its estimation is, besides the state of glass, affected by the experimental parameters [7]. However, the methods offer useful data, at least relative values of T_g of studied glasses in given experimental conditions. Consequently, numerous information about the synthesis conditions and about the usefulness of synthesized glasses can be achieved.

Results and discussion

The results (Figs 1, 2) distinguish two temperature intervals with different characteristics of thermal stability, where 400°C is the temperature dividing these two intervals. The undoped glass does not undergo mass changes under heating upto 400°C, doped glasses display the mass decrease (0.5–2.0%) in this temperature region. The mass decreases evidenced from TG curves of doped glass samples indicate the presence and decomposition of pollutants in glasses. These represent in the studied system:

(i) decomposition of halides, mass decrease 0.5–2% reaching its maximum rate at around 250°C, and

(ii) decomposition of sulfides, mass decrease 0.5–1% reaching maximum rate at 200°C.

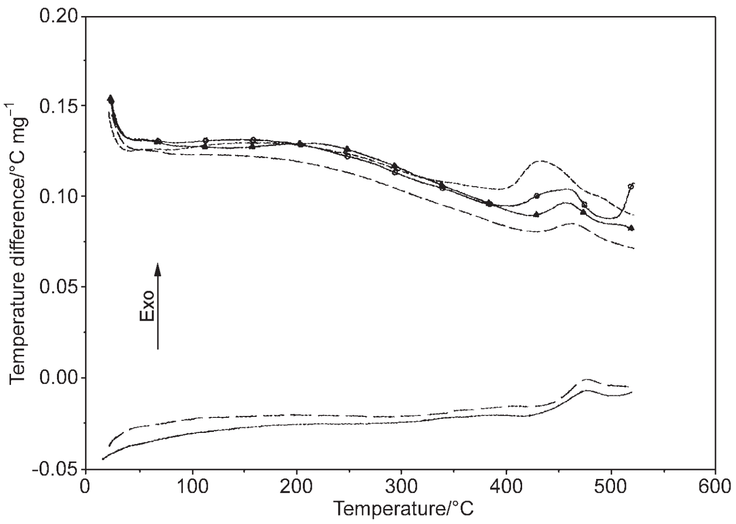

Fig. 1 Influence of the content and form of dopand upon the DTA curves of the $Ge_{25}Ga_{10}S_{65}$ glasses. T_g values, as calculated from the shape of the curves in the temperature region from 460 to 490°C by the TA 3100 analytical programs software, are given in Table 1

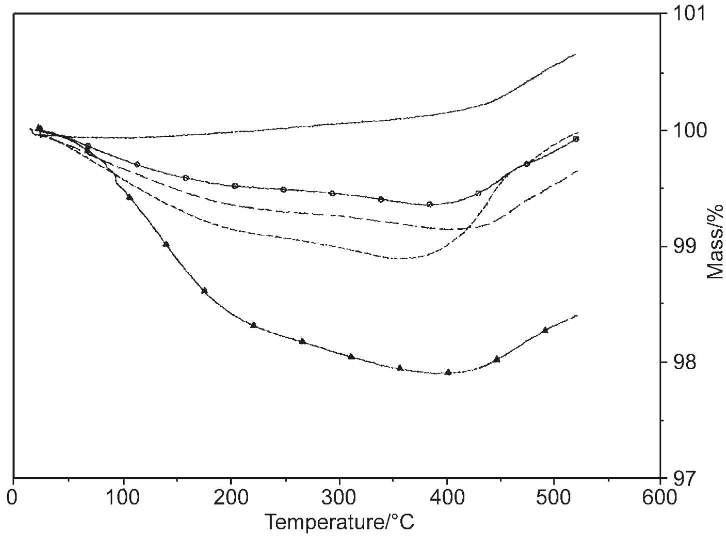

Fig. 2 Influence of the content and form of dopand upon the TG curves of the $Ge_{25}Ga_{10}S_{65}$ glasses

The second temperature interval, 400–500°C is characterised by the mass increase 0.5% or 0.5–1% of undoped or doped glasses respectively. DTA curves exhibit the exoeffects with maxima at 470 or 400–500°C of undoped or doped glasses respectively. The events in this temperature interval we attribute, similarly as in [6], to the glass transition of the studied glasses, the shifts of T_g values are discussed below.

Table 1 Effect of the content and form of dopand upon the Δm a T_g values in $Ge_{25}Ga_{10}S_{65}$ glasses

Sample		Thermoanalytical characteristics from 400 to 500°C	
Labelled	Composition	Δm/%	T_g/°C
GS	$Ge_{25}Ga_{10}S_{65}$	0.5	470
GS 0.5 P(S)	$Ge_{25}Ga_{10}S_{65}$ with 500 ppm Pr in sulfide form	0.9	490
GS 3 P(S)	$Ge_{25}Ga_{10}S_{65}$ with 3000 ppm Pr in sulfide form	0.4	489
GS 6 P(S)	$Ge_{25}Ga_{10}S_{65}$ with 6000 ppm Pr in sulfide form	0.3	472
GS 1 P(H)	$Ge_{25}Ga_{10}S_{65}$ with 1000 ppm Pr in halide form	0.4	481
GS 3 P(H)	$Ge_{25}Ga_{10}S_{65}$ with 3000 ppm Pr in halide form	0.4	483

The changes of materials characteristics in temperature interval 400–500°C are of key interest. DTA events and mass changes (Table 1) enable to define:

1. Glass transition, dependence of T_g values upon the presence and form of dopand;

• Undoped glass $Ge_{25}Ga_{10}S_{65}$ – T_g =470°C

• Glass with Pr in form of halides – T_g =480–485°C, the effect of the amount of dopand is not followed statistically.

• Glass with Pr in form of sulfides – T_g =470–490°C, the shift of T_g value is inversely proportional to the amount of dopand.

2. Non-stability of glass against the oxidation in this temperature region; Δm=0.5–1.0% being evidently the consequence of the effect of air atmosphere upon the glassy skeleton at temperatures close to the glass transition.

The results showed the dependence of glass transition upon the presence and content of dopand as well as the substantial effect of the form of dopand – chemical nature of compound from which the doping Pr atoms are incorporated into the glass. Similarly this dependence is reported in [6]. The comparison of the intervals of shifts of T_g values confirms that the values are affected so by the nature of glass so by the experimental parameters of DTA or DSC methods [7]. In the studied range of doping by sulfides of praseodymium; T_g values get closer to the T_g value of undoped glass with the increased content of the dopand as the results of close stoichiometry in both undoped as well as doped glasses. Inverse proportionally of the shift of T_g value to the content of Pr–S dopand resembles the bonding of atoms of praseodymium as well as atoms of sulfur during the doping in glasses. The case of doping by halides of praseodymium is different; exclusively Pr atoms are fixed in the glass, the halide component is vitrified and the stoichiometry is anion deficient in the studied range of doping. The possibility of compensation of this deficiency by the oxidation at temperatures around the glass transition is marked in TG curves (Fig. 2) – increase of mass (0.5–1.0%) in the temperature region 400–500°C.

Conclusions

- Temperature of glass transition (T_g) of the $Ge_{25}Ga_{10}S_{65}$ glass in the air atmosphere, as estimated by DTA method, is 470°C.
- $Ge_{25}Ga_{10}S_{65}$ glasses doped *in situ* by 500–6000 ppm of Pr exhibit the dependence of temperature of glass transition upon the quantity and form of dopands, T_g values fall between 460 to 490°C.
- Studied glasses are slightly oxidized in the temperature region of glass transition, thermogravimetric mass increase in the air atmosphere ranges from 0.5 to 1.0%.

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