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Luminescence and Light Scattering in the Doped ZBLAN and Tellurite Glasses

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Some ZBLAN glasses doped with NdF_3 and the tellurium-containing glass $90TeO_2$–$10PbO·P_2O_5$ were studied by physical chemical methods. The temperature dependence of luminescence intensity was obtained for the ZBLAN glasses. Light scattering of ZBLAN glasses and the tellurium-containing glass was studied. The luminescence maximum (1054 nm, Nd) and the scattered light maximum (1100 nm) were recorded in the temperature range 25–440°C for the ZBLAN glasses and 25–530°C for the tellurium-containing glass. The correlation was found between temperature changes in the optical characteristics and data of differential thermal analysis of the glasses. It was shown that in the optical temperature dependences there were observed changes in the area of glass transition temperature T_g, the onset of crystallization T_x and maximum crystallization T_c. It is possible to use the temperature dependences of optical curves as a control for heat treatment of vitreous samples at glass ceramics production.

Keywords: ZBLAN glasses, tellurium-containing glasses, luminescence, light scattering, DTA, glass ceramics.

Introduction

Glassy materials activated by the rare earth elements (RE) are used as an active medium to create lasers, fiber amplifiers, luminescent sensors. The most promising materials are activated glass-ceramics [1-3]. Typically, glass-ceramics is obtained by spontaneous crystallization, i.e. the crystal nanosize phase in the bulk glass is produced under exposition at temperatures slightly above the glass transition temperature T_g [4-6]. The REs in the crystal composition are as nucleation sites [7, 8].

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Glass ceramics refers to the intermediate position between crystals and glasses. It combines the best properties of crystals – high mechanical and thermal strength – and the best characteristics of glasses – the possibility of pressing and forming, the ability of extending of optical fiber and carrying out the ion exchange to create waveguide structures [4].

To produce glass ceramics it is necessary to control the crystallization process directly during the heat treatment to be able to stop heating at the desired step. Therefore, the purpose of this work is to study the temperature dependence of spectra of luminescence and scattered light versus thermal properties of the glasses.

Materials and methods

For synthesis of glass samples there were used tellurium oxide TeO_2, fluorides of zirconium ZrF_4, barium BaF_2, aluminium AlF_3, lanthanum LaF_3,ytterbium ErF_3, and neodymium NdF_3 of the "pure" grade, lead metaphosphate $Pb(PO_3)_2$ of the "pure for analysis" grade. The dried initial reagents were milled by a Retsch vibration mill MM 301 for 30 minutes with frequency of 20 beats per minute.

The ZBLAN glass synthesis was done in the covered platinum crucible by the technique "a crucible in a crucible" in the electric furnace of adjustable heating at temperature of 900-950°C for 25–30 minutes. The technique of tellurium glass synthesis was described in [9]. The melt was poured into the steel rings placed on the nickel mold preheated to 220-300°C. Then the surface was quickly evened by the hot press, removing the excess vitreous mass. And finally the melt was cooled to the room temperature.

For research there were used glass powders, pressed into tablets of 2 mm thickness, and transparent glass samples, poured into steel rings with the outer diameter d_{out} = 1.2 cm and thickness of 1-3 mm. The glass surface was smooth enough, so they were not polished additionally.

Differential Thermal Analysis (DTA) spectra of the glass powders were recorded in air on a modernized derivatograph Q–1500 (MOM company) using the covered platinum crucibles at the heating rate of 5°C per minute.

The temperature dependences of luminescence were obtained for the samples, placed in the thermal cell, by irradiating of a xenon lamp DKsSH–150 in the range of 340–700 nm selected by a combination filter SZS23+SZS25. The heating effect on light scattering by the samples was studied at irradiating with light from 800 nm, selected by the filter IKS1. The angle of the excitation light flux on the sample surface was 45°, the angle of the recorded flux – 25°. Intensity measuring of luminescence and scattered light was carried out with continuous registration on a spectrometer SDL–1 at wavelengths 1054 and 1110 nm, respectively. The sample temperature was varied from 25 to 440°C for the ZBLAN glasses and from 25 to 530 °C for the tellurium-containing glasses. The heating rate of samples was similar to the heating rate in DTA and was equal to 5±1 °C/min. The luminescence spectra were recorded directly during the sample heating.

Results and discussion

Compositions of the studied ZBLAN and tellurium-containing glasses are presented in the Table. Temperature dependences of the luminescence intensity (λ = 1054 nm) of the ZBLAN glasses doped with NdF_3 at various thickness of samples are shown in Fig. 1. The curve shapes are somewhat similar to the DTA curves of the glasses at heating. In the range of 261–272 °C, there are observed small

Table. Composition of the studied glass samples

Sample	Glass composition, mol%								
	ZrF_4	BaF_2	LaF_3	AlF_3	NaF	NdF_3	YbF_3	TeO_2	$Pb(PO_3)_2$
ZBLAN–1NdF_3	53	20	3	3	20	1	-	-	-
ZBLAN–1YbF_3	53	20	3	3	20	-	1	-	-
ZBLAN	53	20	4	3	20	-	-	-	-
TeO_2–$Pb(PO_3)_2$	-	-	-	-	-	-	-	90	10

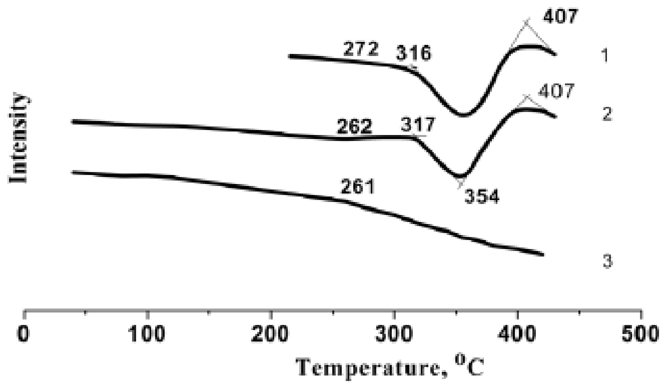

Fig. 1. Temperature dependences of intensity of the neodymium luminescence band (1054 nm) in the ZBLAN–1NdF_3 glass samples of thickness: 1 – 3 mm; 2 – 2 mm; 3 – repeated heating of the sample 2

inflections in the curves. At these temperatures in the ZBLAN glasses, the softening begins, which is characterized by appearing of a little mobility of structural layers and corresponds to the glass transition temperature T_g.

At 354 °C the curves pass through a minimum and go to a maximum at 407 °C. On the DTA curve of the ZBLAN-1NdF_3 glass, these values are close to the temperatures of the first crystallization onset $T_{x1\,=}$ 348 °C and the second crystallization onset $T_{x2\,=}$ 403 °C (Fig. 2). It should be noted that at reheating of the cooled crystallized glass sample ZBLAN-1NdF_3 the luminescence intensity decreases monotonously and does not match the parabolic nature (Fig. 1, curve 3). Consequently, the complex shape of luminescence curves of the original glasses is associated with structural changes at heating process, as the irreversible crystallization is typical for the ZBLAN glasses.

The sample heating was finished at 440 °C to avoid the beginning of melting and flowing of the softened glass mass from the ring-shaped molds. Upon cooling, the luminescence intensity increased monotonously, while there was a slight inflection at 360°C, which corresponds to the crystallization process (the exothermic effect at 360 °C) in the DTA cooling curve. The Nd^{3+} luminescence spectrum shape varies slightly during the sample heating, while the intensity increases about twice in the cooled (crystallized) sample (Fig. 3).

The temperature curves of light scattering by the samples of ZBLAN and TeO_2–$Pb(PO_3)_2$ glasses are shown in Fig. 4. The curve shapes of the ZBLAN glasses (Fig. 4, curves 1–3) are similar in nature, which is explained by the same structure of the ZBLAN glass. In the range of 265–268 °C as well

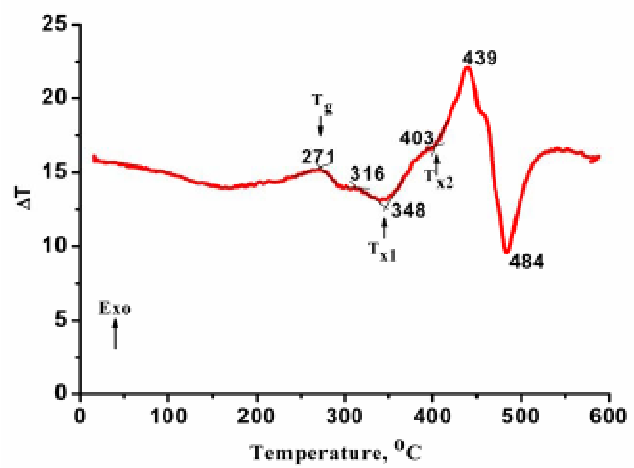

Fig. 2. DTA curve of the glass powder ZBLAN–1NdF_3 recorded at the rate of 5°C/min. in air

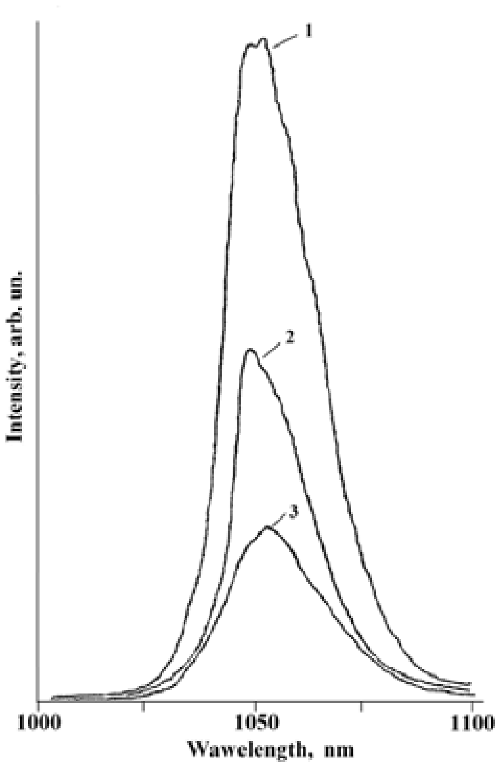

Fig. 3. Evolution of the Nd^{3+} luminescence spectrum shape versus temperature: 1 – after heating to 440 °C and cooling to 23 °C; 2 – before heating, the original sample; 3 – at 440 °C

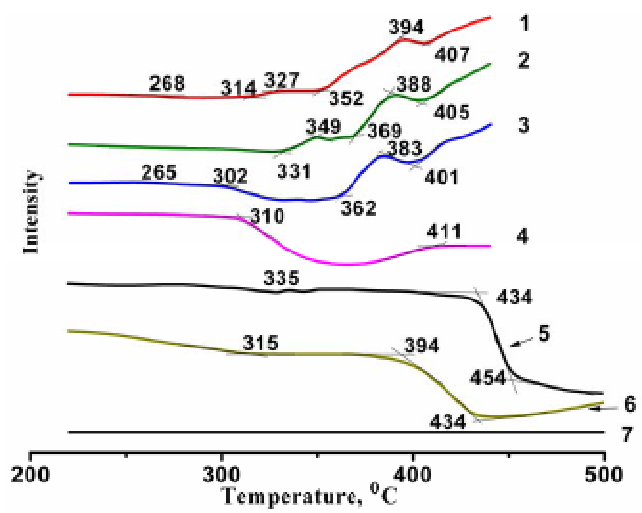

Fig. 4. Temperature dependences of light scattering (λ = 1100 nm) by the samples of thickness: 1 – 2.5 mm, ZBLAN glass; 2 – 2.5 mm, ZBLAN–1YbF_3 glass; 3 – 2.0 mm, ZBLAN–1NdF_3 glass; 4 – 2.0 mm, tablet of the ZBLAN–1NdF_3 glass powder; 5 – 2.0 mm, 90TeO_2–10Pb$(PO_3)_2$ glass; 6 – 2.0 mm, tablet of the 90TeO_2–10Pb$(PO_3)_2$ glass powder; 7 – 2.0 mm, tablet of Al_2O_3

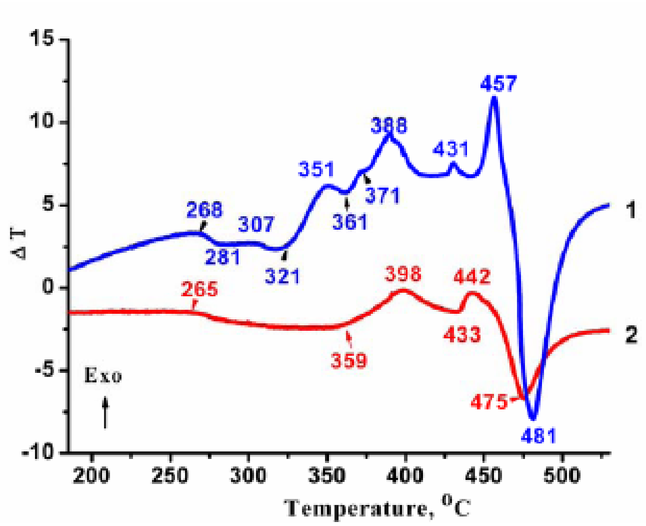

Fig. 5. DTA curves of the ZBLAN glass for the powder (1) and bulk glass poured into the ring with thickness of 2 mm (2), recorded at the rate of 5°C/min. in air

as for the luminescence curves, there are observed slight inflections, that in the differential curve corresponds to the glass softening temperature T_g (Fig. 5).

The curves of light scattering have several minima and maxima, and are more complicated in nature as compared with the luminescence curves. However, one can identify some patterns. Near the temperature range corresponding to the glass transition temperature T_g, there is observed a decrease in the scattering intensity, whereas at temperatures at which crystallization begins, the light scattering intensity increases (Fig. 4). This is well illustrated by the sample ZBLAN–1NdF_3 pressed into a tablet

(Fig. 4, curve 4). An influence of temperature characteristics of the sample on the shape of the scattering and luminescence temperature curves is obvious. This is confirmed by nature of scattering curves of tellurium-containing samples and aluminum oxide.

Thus, for the $90TeO_2$–$10Pb(PO_3)_2$ samples, contrary to the ZBLAN samples, the changes appear much later – in the range of 315–335 °C (T_g – the beginning 324 °C, the end – 347 °C), and up to 400°C for the glass sample (Fig. 4, curve 5) no changes were observed. For the pressed Al_2O_3 sample in the whole heating range from 25 to 530 °C no changes were observed, which is rather understandable. This is a fairly stable compound, $T_{melt.}(Al_2O_3)$ = 2010–2050 °C.

Conclusions

The temperature dependences were studied of luminescence intensity and light scattering for the samples of ZBLAN and tellurium-containing glasses in the temperature ranges of 25–440 °C and 25–530 °C, respectively. The correlation was revealed between temperature changes of intensity maxima of the optical spectra and DTA data of the samples. It was shown that in the optical temperature dependences, there are observed changes in the glass transition temperature T_g, onset of crystallization T_x and the crystallization peak T_c of the glasses. The obtained relations between the sample optical spectra and thermal properties can be used for controlled heat treatment to produce glass ceramics.

Acknowledgements

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Люминесценция и рассеяние света в допированных стеклах ZBLAN и теллуритных стеклах

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Физико-химическими методами изучены некоторые стекла ZBLAN, допированные NdF_3, и теллурсодержащее стекло $90TeO_2$–$10PbO{\cdot}P_2O_5$. Для стекол ZBLAN получена температурная зависимость интенсивности люминесценции. Исследовано рассеяние света в стеклах ZBLAN и в теллурсодержащем стекле. Максимумы люминесценции (1054 нм, Nd) и рассеяния света (1100 nm) определены в диапазонах температур 25–440 °С для стекол ZBLAN и 25–530°С для теллурсодержащего стекла. Обнаружена корреляция между температурными изменениями оптических характеристик и данными дифференциального термического анализа рассмотренных стекол. Показано, что в температурных зависимостях оптических характеристик наблюдаются изменения в области температур стеклования T_g, начала кристаллизации T_x и максимума кристаллизации T_c. Возможно использование температурных зависимостей оптических кривых для контроля термообработки стеклянных образцов при получении стеклокерамики.

Ключевые слова: стекла ZBLAN, теллурсодержащие стекла, люминесценция, рассеяние света, ДТА, стеклокерамика.