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Glass Containing Eu_2O_3, Tb_2O_3, Sm_2O_3, ZnO as a Color Filter used in the Automotive Industry

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Over the next few years, LEDs are likely to be responsible for all of the vehicle's exterior lighting functions. Everything is focused on maximum security. For this reason, there are more and more automatic color detection systems in the car. Proper color separation is the key to optimal operation and proper evaluation of these automatic systems. An example is the correct detection of traffic light colors. The automotive industry is dependent on consistency and predictability. Classification is an important function for automated control and requires the correct color resolution of the signals captured by the cameras. We propose to use glass containing various colored active substances such as Eu_2O_3, Tb_2O_3 and Sm_2O_3 as color filters for LED diodes. LED source from one visible light area to another visible light area. This study is devoted to the production of photoactive glass. Subsequently, the photosensitivity of molten photoactive glasses is tested. Both the absorption and excitation spectra of selected photosensitive glasses are measured.

Keywords: Technology, Automotive, Glass, Color filtres, LED

1 Introduction

1.1 Glass

Glass is a thermodynamically unstable material that lacks translational symmetry over longer distances. The basic structure of glass are silicate tetrahedral networks interconnected by bridge oxygens, deformed by a number of modifiers. At temperatures above the melting point of the crystalline substance, it is in a thermodynamically stable state—melt. With sufficiently fast cooling, the linear dependence of enthalpy on temperature prolongs and the melt turns into a subcooled liquid. After reaching the so-called glass transition temperature, the movement of molecules practically stops, which is reflected in a decrease in viscosity to a value of approximately 10^{13} dPa.s and a deviation from the linear dependence. The glass transition temperature is different for different cooling rates, with glasses that are cooled faster reaching this temperature faster. The thermodynamic instability of glasses is reflected in the so-called transformation interval, ie the temperature range, which is precisely defined by viscosities 10^{12}–10^{15} dPa.s. The degree of stabilization is usually defined by the so-called fictitious temperature, ie the temperature at which the structure of the equilibrium structural configuration of the glass freezes. The further this temperature is from the transformation temperature, the less stable the glass. Glass depends mainly on the cooling rate from the melt. The cooling rate must be large enough not to crystallize. The normal glass cooling rate is approximately 10^{-4} $K.s^{-1}$ [1].

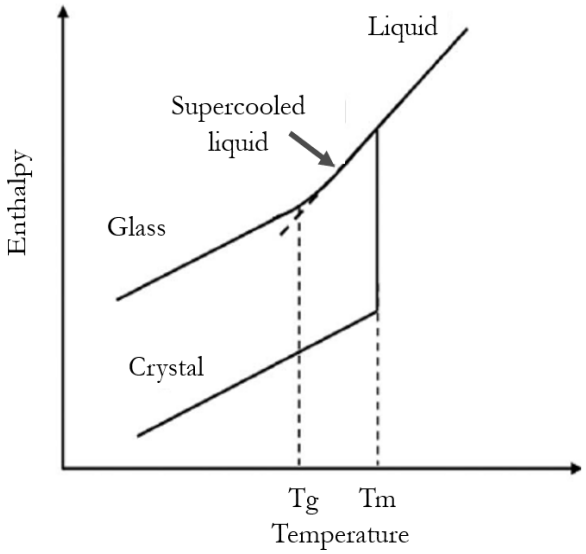


Fig. 1 *Thermodynamic definition of glass – dependence of temperature on enthalpy. When glass is in liquid phase and it is cooled down it became a supercooled liquid that changes into glass in the next step when reaching a glass transition temperature - Tg. The cooling rate of glass is crucial in order to avoid crystalization*

1.2 Optical glass

The most important factor for the preparation of optical glasses is their excellent homogeneity and

precisely defined refractive index and dispersion, which is best characterized by the Abbe number. To melt they use high-purity raw materials, they are most often melted in all-electric resistance furnaces or inductive. High homogeneity is achieved by intensive mechanical mixing of the melt. Semi-finished products similar to the final product are then formed from the molten glass. After cooling down the glass must often be sharpened and polished. Optical glasses are divided into crown and flint glasses according to their composition and special (phosphoric, halide, etc.) [2-3].

The principle of using glass materials in the field of color filters is the modulation of the wavelength of the initial radiation. Modulation is achieved by adding lanthanide and other oxides to the glass stem. The oxides samarium, erbium and europium are most often used here. These oxides usually absorb the blue or green radiation of the source and convert it to the red region of the spectrum. The most important fact in the preparation of glass wavelength modulators (hereinafter samples) is their high luminescence. Glass samples are sodium-silicate glasses with a high content of zinc oxide with the composition: SiO_2 – Na_2O – ZnO – Al_2O_3 – Eu_2O_3 (Tb_2O_3, Sm_2O_3). Tab. 1 describes the weight of raw materials for the production of sample L1 with a content of 4.25 wt. % Eu_2O_3 and 13.53 wt. % ZnO.

Tab. 1 *Composition of glass L1 with adddion of Eu_2O_3*

Glass L1 with Eu_2O_3	
Compound	Mass (g)
Na_2CO_3	9.65
ZnO	6.37
$Al(OH)_3$	0.63
SiO_2	28.29
Na_2SO_4	0.13
Eu_2O_3	2.01

There are several models that describe the mechanism of photosensitivity. One of them, the so-called color center model (example in fig. 2), says that photosensitivity in optical glasses can be judged by individual absorption bands. Precursors and products of photochemical processes can be deduced from the intensities of the absorption bands. This model has been elucidated on doped glass fibers germanium. Another model, the so-called stress relaxation model, defines the change in refractive index as a consequence of the persistent stress in the glass. Stress in glass is most often created during technological processing, especially when it is cooled too fast [4].

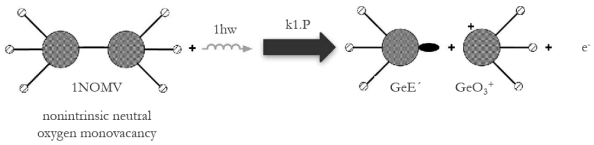


Fig. 2 *Photosensitivity Color-Center Model example of Ge-Doped Silica Preforms*

1.3 Optical glass forming components

1.3.1 Silica

Silica is the cross-linking oxide of the vast majority of glasses. Quartz glass is glass made of pure quartz and consists only of silica of regular structure. This is glass with very low thermal expansion and very good chemical resistance. Quartz glass is permeable to UV radiation and very permeable to IR radiation. Its problem is difficult melting, which is reflected in the subsequent price of such glass. Another problem is its low index break. For this reason, refractive index modifiers must be added to the quartz glass like substances that are able to increase the refractive index, such as GeO_2, ZrO_2. Quartz glass is thanks its properties, mainly due to the low damping in the IR region, an excellent material for fiber optic design [2].

1.3.2 Zinc oxide

Oxides that increase the photosensitivity of glasses include, for example, GeO_2, B_2O_3, SnO_2 or ZnO. The most interesting properties appear to be zinc oxide, which significantly enhances the resulting luminescence at passage of radiation through samples. It has been observed that with increasing zinc oxide content in glass, its resulting luminescence also increases [4].

1.3.3 Oxides enabling wavelength change – lanthanoides

To change the wavelengths, we use lanthanide oxides Eu_2O_3, Tb_2O_3 and Sm_2O_3, which can absorb blue and green light respectively and convert it to the red region of the spectrum. This phenomenon can be used in the production of glass samples – solid-state color filters for LEDs sources.

1.4 LED principle

An LED, or luminescent diode, is a semiconductor device that contains a PN junction, and which emits electromagnetic radiation in the forward direction when connected to a voltage source. It's acting is a direct converter of electrical energy to optical radiation. This radiation is almost monochromatic and is not coherent. The LED can produce radiation in the infrared, visible and ultraviolet spectrum regions (350-1100 nm). The great advantage of LEDs is their long life and high efficiency. $A^{III}B^{V}$ type semiconductors are mainly used to create PN semiconductor junctions IN

high purity, which can be alloyed with a small amount of suitable additives. Ingredients serve either to generate an excess of electrons like an N-type material, or vice versa holes, ie material of type P [5].

1.5 Lasers

After LEDs, lasers are the most common source used for detection. The principle of the laser lies in its use stimulated radiation emissions. It is based on the amount of energy that hits the atom in the excited state and which is equal to the energy difference of the considered levels, is not absorbed, but two quanta of the same energy are created (light radiation of double energy is created) [6]. Their great advantage is that they produce monochromatic coherent radiation, which it allows considerable flexibility for the usage in the automotive industry. Organic solutions have been invented that is able to change the wavelength of the source. Such lasers are called DYE lasers. However, organic solutions are unsuitable in terms of time stability and therefore it is, more practical to choose another material that would prove organic solutions prospectively the use of glass samples which are capable of absorbing radiation of a certain wavelength; andemit radiation of different wavelength [7].

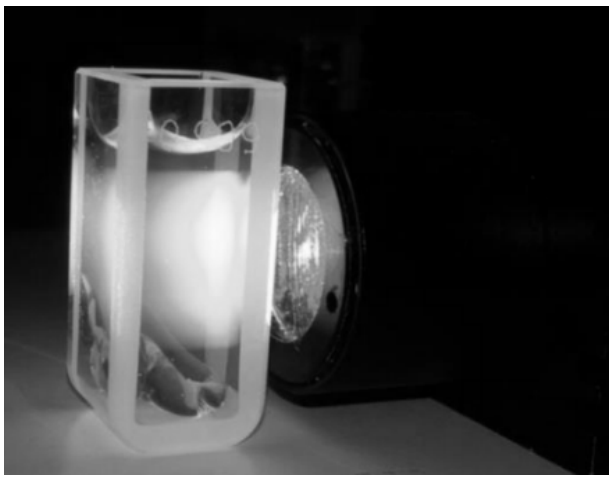


Fig. 3 *Stimulated emission of a photosensitive substance induced by a green laser with a given wavelength of 532 nm*

1.6 Lamps

Lamps are a source of light that produces incoherent radiation. It is a source radiating in a wide range of wavelengths. The use of lamps continues to this day, some cars use so-called xenon lights. Light is created by the discharge between two electrodes between two electrodes in the environment of xenon vapors. Xenon lamps, as a source, it is necessary to use ballast filters that transmit only light of the selected wavelength. The advantage of these lamps is the fact that they can work in pulse mode and are cheap compared to other sources [8, 9].

1.7 Solid-state lasers

Other light sources include solid-state lasers, the environment of the so-called Nd: YAG garnet laser is formed by an isotropic YAG crystal (Y3Al5O12) doped with Nd3+ ions. The color of the crystal is pink to purple depending on the amount of doped Nd3+. This crystal is excited, for example, by a xenon lamp. This source operates in continuous or pulse mode. The maximum wavelength that can be achieved with this laser is 1064 nm. Lower wavelengths can also be emitted, which results in lower efficiency of the emitted radiation [10].

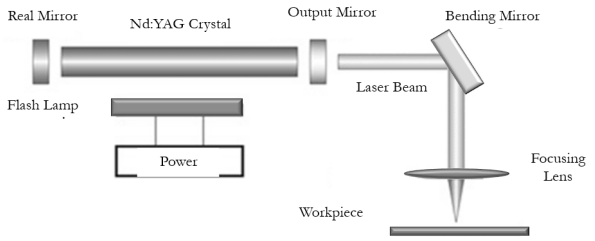


Fig. 4 *Solid state lasers configuration using Nd:YAG Crystal*

1.8 Laser diodes

Laser diodes can generate monochromatic coherent radiation with low divergence. The function of the laser diode is based on stimulated emission. The active environment of this laser forms the surroundings of the PN junction. An important parameter of the laser diode related to stimulated emission is the so-called threshold current (or threshold voltage). In order for the laser diode to work as it should, a current greater than the threshold must flow in the forward direction. If this condition is not met, the laser diode will behave like an LED (wide, non-monochromatic radiation of low intensity). Below the threshold current, only spontaneous emission occurs, and thus non-coherent radiation is generated. Conversely, if the current value is higher than the threshold value, the diode power increases sharply and stimulated radiation emission occurs, resulting in coherent radiation. Threshold current values are normally in the range of 40–250 mA (threshold voltage is around 1.8 V), however, the threshold current value is highly temperature dependent [11].

1.9 Usage of LEDs in the automotive industry

One of the most promising direction for improving the level of traffic safety is various active safety systems creation. This area is intensively developed by leading foreign automakers and it is not complete. The relevance of researches aimed at effective active safety systems creating is determined by the world importance level of the traffic safety

problem. Current study aims at the scientific substantiation of new technical solutions for the integrated vehicle active safety intelligent system [12]. The detection systems of obstacles on the road are based on the precise detection. For this reason, there are more and more automatic color detection systems in the car. Proper color separation is the key to optimal operation and proper evaluation of these automatic systems. Traffic light classification is an important feature for automated driving, and it requires correct color separation of the traffic lights signals captured using cameras. A key camera component for the color separation performance is the color filter array (CFA). For common automotive-specific CFAs, we have observed unsatisfactory performance for TL color separation, which indicates the need for an optimization.

Color filters may play an interesting role in the detection improvement [13]. There are more and more autonomous systems in the development. Another examples is a model and control algorithms for traction and brake channels are based on deterministic descriptions of traction, braking acceleration and course angle determined by control actions on the controls [12]. Another example of potential usage of color filters is the vehicle deceleration light signalling system. Based on global statistics on the number of road accidents caused by non-compliance with the safety distance and a market research on the availability of purchasing an extra option to allow drivers to be informed about the speed reduction of the vehicle in front [14]. Another example is an augmented reality based windshields in a car regards to them we can see the information projected directly on the windshield. Another option is that digital images can be projected directly into objects [15-17].

2 Experiment

2.1 Preparation of mixture

Tab. 2 *Components used to melt the glass*

Compound	Producer	Moisture content (%)
SiO_2	Fluka	1.67
Na_2CO_3	Penta	1.61
Al_2O_3	Merk	4.93
ZnO	Lach-Ner	0.07
Na_2SO_4	Penta	1.50
Eu_2O_3	Sigma-Aldrich	0.01
Sm_2O_3	Sigma-Aldrich	0.01
Tb_2O_3	Sigma-Aldrich	0.01

The glass raw materials are weighed and subsequently homogenized in a mortar. The mixing of the raw materials takes place for 10 minutes. The homogenization of the glass powder components occurs due to the mixing of the weighted components in the mortar using the pestle. The composition of the powders used for melting is described in tab. 2.

2.2 Melting process

The sample is then placed in a PtRh crucible. Melting took place for two hours in a supercantal electric furnace at a temperature of 1530 °C. After one hour, the sample is mixed and then the mixing is repeated at 15 minutes intervals. The melt is mixed a total of five times. The sample is cast in a stainless steel mold and allowed to cool in a cooling oven at 560 °C to release stress from the final product. The sample is left in the cooling oven overnight. It is then cooled to room temperature in a controlled manner. Defined shapes of glass samples are cut from a glass lump on a diamond saw, which are then ground and polished. The added lanthanide oxides are described in Tab. 3.

Tab. 3 *Oxides enabling wavelength change – samples L1-L3.*

L1	L2	L3
Eu_2O_3	Eu_2O_3	Eu_2O_3
	Tb_2O_3	Sm_2O_3

The melting furnace used is shown in Figure 5. You can also see the crucible with the sample before the mixture was mixed. The crucible already has a molten mixture at a temperature greater than 1500 °C.

Fig. 5 *Glass melting furnace for the production of photoactive glass – samples L1-L3*

The color of the resulting luminophores is primarily determined by the composition of the glass that entered the melting process. It is mainly due to the components that are able to color the glass, the so-called dyes. In our case Eu_2O_3, Tb_2O_3, Sm_2O_3. The homogeneity of the glass, i.e. its properties, is determined by the regular mixing of the glass at given time intervals (Fig. 6).

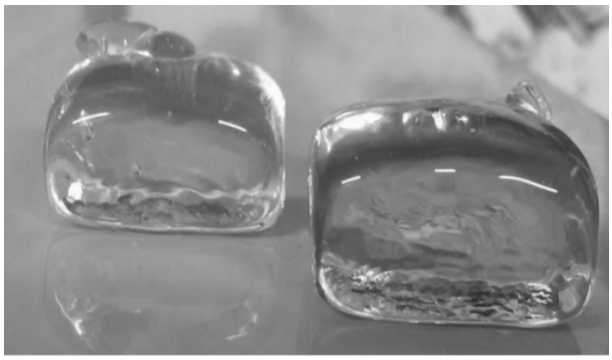


Fig. 6 *Molten glass from which glass samples are carved and ground*

The manufactured glasses are experimentally examined using the methods described in section 3 - measurement. Manufactured glasses absorb radiation of a given wavelength and emit radiation of a wavelength in a different interval of the visible spectrum. The composition of glasses and the addition of specific oxides have a direct effect on the region of the spectrum in which the given glass absorbs incoming radiation from the source and emits radiation at a different wavelength. The goal is to design the composition of the glass so that the glass absorbs the highest possible amount of radiation at a given wavelength of the source and induces intensive emission in a different region of the spectrum. In Figure 7 we see an example of the excitation of glass L1 with a blue laser with a wavelength of 405 mm. The radiation passes from the blue region of the spectrum to the red region of the spectrum.

Excitation of the glass left in the PtRh crucible after melting of L2 (Fig. 8).

In Figure 9, you can see an example of a luminophore that was cut from a fused glass sample, which is inserted into the laser plane and its role is to modify the wavelength of the source.

Fig. 7 *An example of L1 glass excitation by blue laser with 405 mm wevalength*

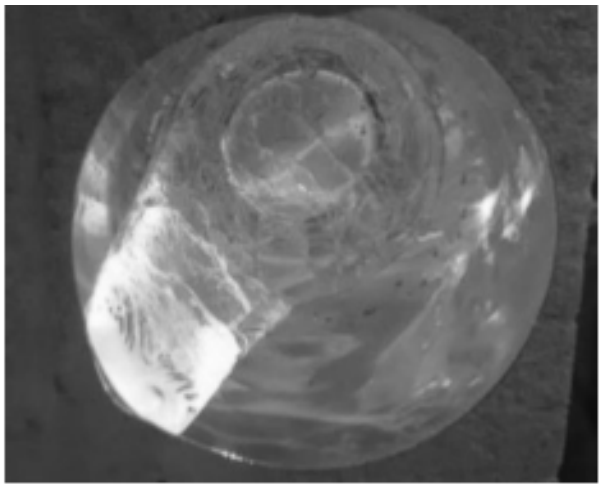


Fig. 8 *An example of L1 glass excitation by blue laser with 405 mm wevalength*

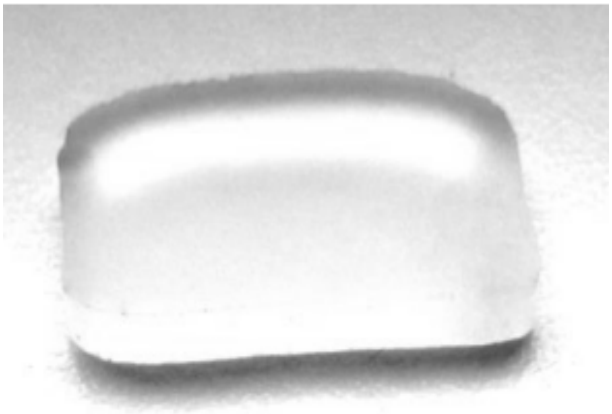


Fig. 9 *An example of L2 glass cut into piece*

3 Measurement

3.1 Measurement of glass absorption spectras

To measure the spectra, 3 glass samples are selected, namely glass samples L1, L2 and L3. The absorption spectra of all samples are measured on a Shimadzu UV-1601 spectrophotometer. The Shimadzu UV-1601 UV-VIS Spectrophotometer is a high performing, double beam spectrophotometer with a spectra wavelength range of 190 to 1100 nm. The spectrophotometer has a scanning speed between 3200 nm/min to 160 nm/min.

During the analysis, the spectrophotometer compares the intensity of the radiation emitted by the source with the intensity of the radiation falling on the detector - part of the energy of the light radiation is absorbed by the solution and dissolved substances. The amount of absorbed radiation is then proportional to the concentration of the substance in the studied solution. In this case, the sample is a glass sample that is excited by a defined source of a given wavelength (Fig. 10).

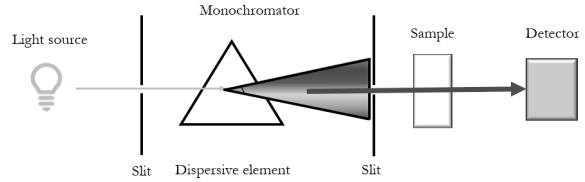


Fig. 10 *Schematic configuration of UV-VIS spectrophotometer*

Based on the measured absorption spectra, we can select sources with a suitable wavelength. The absorbance depending on the wavelength is plotted against the dependence of the measured substances.

3.2 Measurement of glass emission /excitation spectras after laser / LED irradiation

The emission spectra of selected photosensitive substances were measured. The source is a laser / LED of defined wavelength. A Nikon E 400 Pol microscope with a Nikon digital camera (max. Resolution 2560 x 192 px) is used for luminescence measurements. The Nikon microscope is also equipped with an OscanOptics SD 2000 spectrometer, which allows objective color comparison of different points. The Philips Focus halogen-tungsten projection lamp is used as the source in the microscope 43 Line (6 V, 30 W). The radiation passing through the sample is detected on the detector, resulting in a luminescence spectrum. A laser with a source wavelength of 405 nm with a power of 20 mW.cm-2 was used to measure the more intensive spectrum.

The glass sample was measured with a Nikon microscope under laser excitation. A laser of a defined wavelength shined on the sample, causing excitation of the sample radiation. The sample absorbs in the blue light region and emits in the red region of the spectrum (Fig. 11).

Fig. 11 *Schematic configuration of glass emission measurement using Nikon E 400 Pol*

4 Results

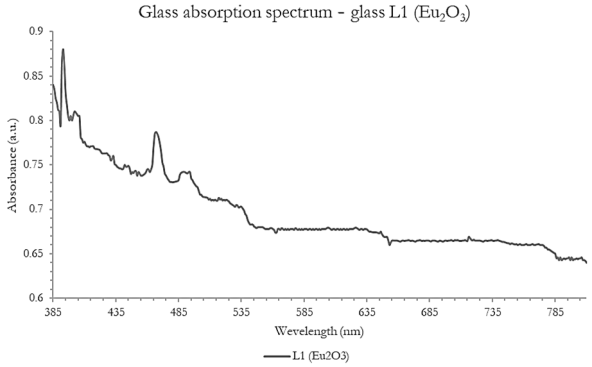
4.1 Measurement of glass emission /excitation spectras after laser / LED irradiation

Absorption spectra were measured for each glass sample L1, L2 and L3, which will allow choosing a suitable source of radiation and a suitable wavelength. The source can be selected according to the position of the peak with the highest absorption intensity.

In code chapters 4.1.1 to 4.1.3 you can see the measured absorption spectra according to the description of the instrumentation in point 3.1. In subsection 4.1.4 you can see a comparison of absorption spectra for individual samples 4.1.1 to 4.1.3.

4.1.1 Measurement of the absorption spectrum of sample L1 (Eu_2O_3)

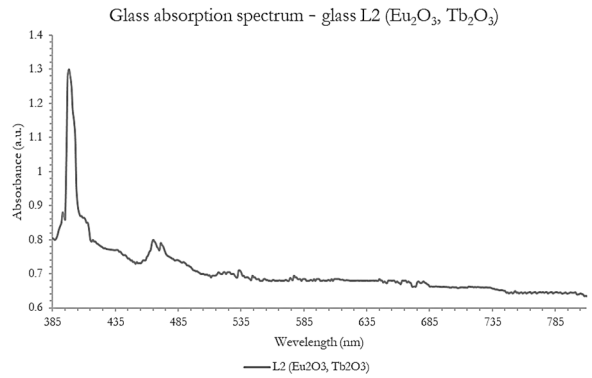
Glass L1 absorbs in the blue region of the spectrum at wavelengths of 405 nm and 470 nm. The highest intensity of absorption is visible precisely at a wavelength of 405 nm (Graph 1).



Graph 1 *L1 glass absorption spectrum – Eu_2O_3*

4.1.2 Measurement of the absorption spectrum of sample L2 (Eu_2O_3, Tb_2O_3)

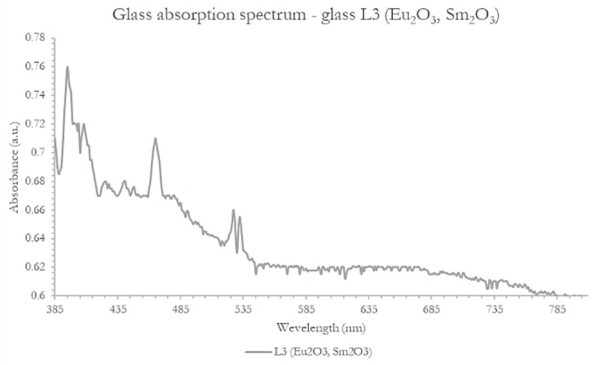
Glass L2 absorbs in the blue region of the spectrum at wavelengths of 405 nm, 465 nm and 470 nm. The highest intensity of absorption is visible at a wavelength of 405 nm (Graph 2).



Graph 2 *L2 glass absorption spectrum – Eu_2O_3, Tb_2O_3*

4.1.3 Measurement of the absorption spectrum of sample L3 (Eu_2O_3, Sm_2O_3)

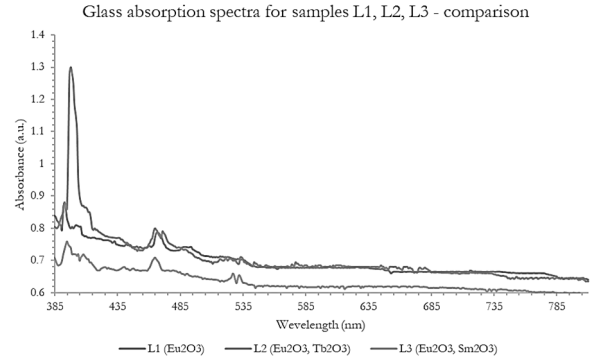
Glass L3 absorbs in the blue region of the spectrum at wavelengths of 405 nm, 470 nm and between 525 and 535 nm. The highest intensity of absorption is visible at a wavelength of 405 nm (Graph 3).



Graph 3 *L3 glass absorption spectrum – Eu_2O_3, Sm_2O_3*

4.1.4 Measurement of the absorption spectra – comparison of samples L1, L2, L3

For all 3 luminescent glasses, the length of 405 nm was chosen as the appropriate wavelength of the excitation source, at which the given glasses show the highest intensity of radiation absorption. Sample L2 shows the highest intensity of absorption of radiation with a given wavelength of 405 nm, on the other hand, sample L3 shows the lowest intensity of absorption at a given wavelength (Graph 4).



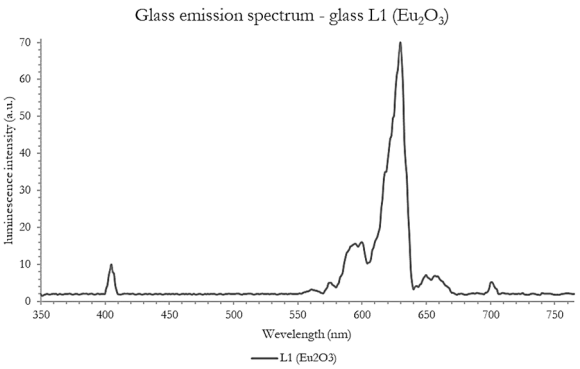
Graph 4 *Comparison of glass absorption spectra of L1, L2, L3 glass samples*

4.2 Measurement of glass emission spectras after irradiation by laser 405 nm

The emission spectra of the given glasses L1, L2 and L3 were measured as described in subsection 3.2. For radiation excitation, a suitable laser according to chart 4 with a wavelength of 405 nm was used, at which the most intensive absorption of radiation by the laser occurs. After laser radiation with a wavelength of 405 nm passes through the sample, we expect stimulated emission of glass radiation, while the wavelengths will shift and the glass will emit in a different region of the spectrum, while we expect the highest intensity of glass radiation after laser excitation in the red region of the spectrum. The given emission spectra are measured in subsections 4.2.1 to 4.2.3. In subsection 4.2.4 there is a comparison of the emission spectra for the given three glass samples L1, L2 and L3. For a given glass sample, the wavelength at which the glass emits and the resulting color of the radiation are found. The given color is shown in the color chart.

4.2.1 Measurement of the emision spectrum of sample L1 (Eu_2O_3)

The glass L1 is excited by the source and induces an intense emission of radiation at 630 nm, which represents an intense emission in the red region of the spectrum (Graph 5, Fig. 12, Tab. 4). The measured intensity of emitted radiation represents 70 relative units.



Graph 5 *Emission spectrum of L1 glass – Eu_2O_3*

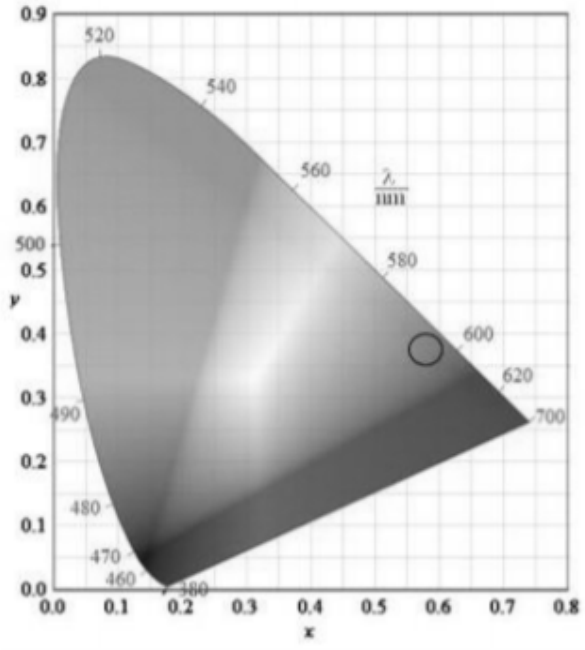


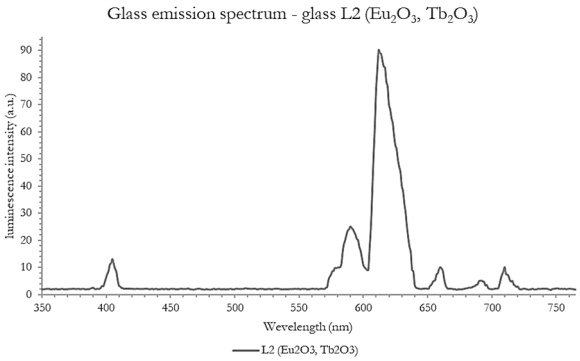
Fig. 12 *Color of for L1 glass – Eu_2O_3*

Tab. 4 *Spectral values of L1 glass – Eu_2O_3.*

Parameter	x	y	u´	v´
Value	0.551	0.376	0.368	0.457

4.2.2 Measurement of the emision spectrum of sample L2 (Eu_2O_3, Tb_2O_3)

The glass L2 is excited by the source and induces an intense emission of radiation between 620 and 630 nm, which represents an intense emission in the red region of the spectrum (Graph 6, Fig. 13, Tab. 5). The measured intensity of emitted radiation represents more than 90 relative units.



Graph 6. *Emission spectrum of L2 glass – Eu_2O_3, Tb_2O_3*

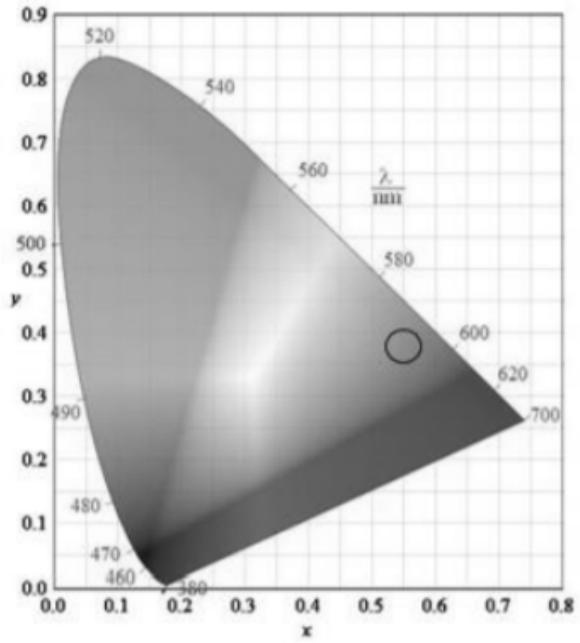


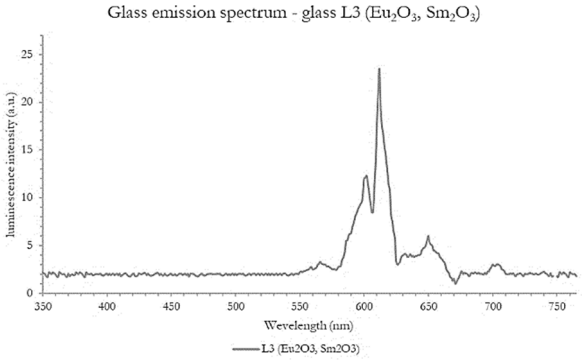
Fig. 13 *Color of L2 glass – Eu_2O_3, Tb_2O_3*

Tab. 5 *Spectral values of L2 glass – Eu2O3, Tb2O3*

Parameter	x	y	u´	v´
Value	0.370	0.547	0.354	0.436

4.2.3 Measurement of the emision spectrum of sample L3 (Sm_2O_3, Tb_2O_3)

The glass L3 is excited by the source and induces an intense emission of radiation between 600 and 620 nm, which represents an intense emission in the red region of the spectrum (Graph 7, Fig. 14, Tab. 6). The measured intensity of emitted radiation represents more than 25 relative units.



Graph 7 *Emission spectrum of L3 glass – Eu_2O_3, Sm_2O_3*

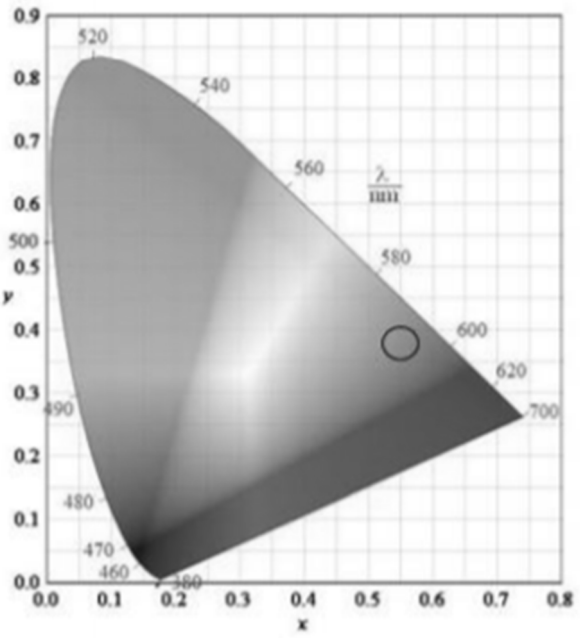


Fig. 14 *Color of L3 glass – Eu_2O_3, Sm_2O_3*

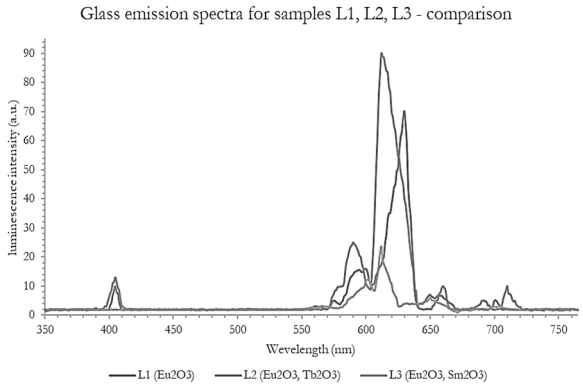
Tab. 6 *Spectral values of L3 glass – Eu_2O_3, Sm_2O_3*

Parameter	x	y	u´	v´
Value	0.575	0.379	0.355	0.422

4.2.4 Measurement of the emision spectra – comparison of samples L1, L2, L3

In graph 8 we see a comparison of the emission spectra of selected glasses L1, L2 and L3. All fused glasses show intense absorption at a source wavelength of 405 nm and emit in the red region of the spectrum between 600 nm and 630 nm. Sample L1 emits radiation in the spectral region with the highest wavelength of 630 nm. Sample L2 emits radiation in the spectral region between 620 nm and 630 nm, showing the highest relative intensity of emitted radiation at a given wavelength, namely 90 relative units.

Sample L3 emits in the region of radiation with the lowest wavelengths among the selected glass luminophores, at a wavelength of 600 to 620 nm, and the intensity of emitted radiation is the lowest, namely 25 relative units (Graph 8).



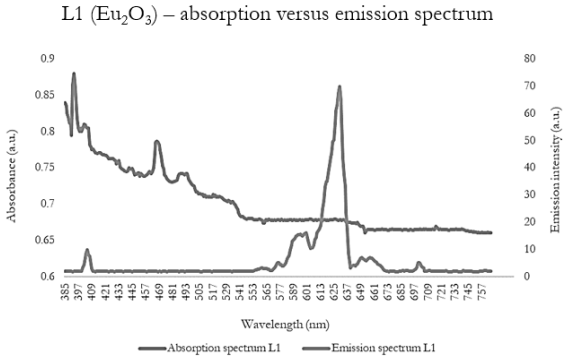
Graph 8 *Comparison of glass emission spektra of L1, L2, L3 glass samples*

4.3 Comparison of absorption and emission spectra of samples L1, L2, L3

The absorption spectra and emission spectra are compared for the individual glass samples L1, L2 and L3. The results for individual glasses are plotted in subsections 4.3.1 to 4.3.3.

4.3.1 Comparison of absorption and emission spectra of sample L1 (Eu_2O_3)

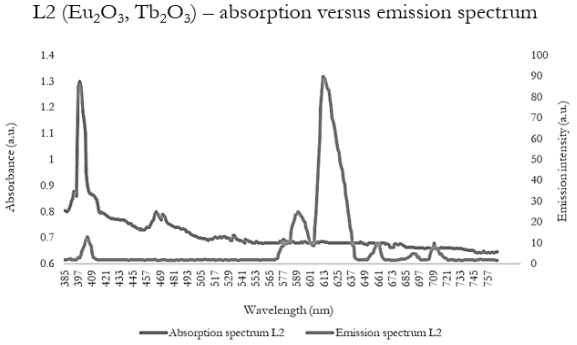
Graph 9 shows a comparison of the absorption and emission spectrum of glass luminophore L1, including wavelengths and intensity of absorbed and emitted radiation in relative units. Luminophore L1 absorbs in the blue region of the spectrum at wavelengths close to 400 nm and emits at wavelengths greater than 600 nm with a relative emission intensity corresponding to the given wavelength of emitted radiation located in the red region of the spectrum. The glass phosphor is usable for converting blue radiation into red with the longest provided wavelength of emitted radiation having a wavelength of 630 nm.



Graph 9 *Absorption versus emission spectra of L1 glass (Eu_2O_3)*

4.3.2 Comparison of absorption and emission spectra of sample L2 (Eu_2O_3, Tb_2O_3)

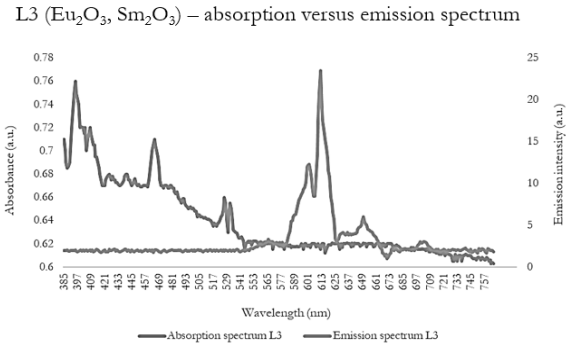
Graph 10 compares the absorption and emission spectrum of glass luminophore L2, including wavelengths and intensity of absorbed and emitted radiation in relative units. Luminophore L2 absorbs in the blue region of the spectrum at wavelengths close to 400 nm and emits at wavelengths greater than 600 nm with a relative emission intensity corresponding to the given wavelength of emitted radiation located in the red region of the spectrum. The glass phosphor is usable for converting blue radiation to red with a wavelength between 620 and 630 nm with the highest relative emission intensity of the 3 samples provided.



Graph 10 *Absorption versus emission spectra of L2 glass (Eu_2O_3, Tb_2O_3)*

4.3.3 Comparison of absorption and emission spectra of sample L3 (Eu_2O_3, Sm_2O_3)

Graph 11 compares the absorption and emission spectrum of glass luminophore L3, including wavelengths and intensity of absorbed and emitted radiation in relative units. Luminophore L3 absorbs in the blue region of the spectrum at wavelengths close to 400 nm and emits at wavelengths greater than 600 nm with a relative emission intensity corresponding to the given wavelength of emitted radiation located in the red region of the spectrum. The glass phosphor is usable for converting blue radiation to red with a wavelength between 600 and 620 nm with the lowest relative emission intensity of the 3 samples provided.



Graph 11 *Absorption versus emission spectra of L3 glass (Eu_2O_3, Sm_2O_3)*

5 Discussion

The L1 sample containing Eu2O3 has the highest absorbance value of 0.88 a.u. at wavelengths 395 - 405 nm. At this wavelength, the highest absorbance of the incoming radiation occurs. The lower absorbance rate is visible at 455 - 465 nm, where a peak with an intensity of 0.78 a.u. The sample L2 containing Eu2O3 and Tb2O3 has a highest absorbance value of 1.30 a.u. at wavelengths 395 - 405 nm. At this wavelength, the highest absorbance of the incoming radiation occurs. The lower absorbance rate is visible at 455 - 475 nm, where two peaks with an intensity of 0.80 a.u. for the first peak and 0.79 a.u. for the second peak. Sample L3 containing Eu2O3 and Sm2O3 has the highest absorbance value of 0.76 a.u. at wavelengths 395 - 405 nm. At this wavelength, the highest absorbance of the incoming radiation occurs. The lower absorbance rate is visible at 455 - 465 nm, where a peak with an intensity of 0.715 a.u. The other two less intense peaks are located in the wavelength range 495 - 525 nm, where the relative absorbance rate is 0.65 a.u - 0.67 a.u. Comparing all the absorption spectra of the glass phosphors produced, we conclude that the highest absorbance rate is 1.30 a.u. for L2 phosphorus encompassing Eu2O3 and Tb2O3 in the region of 395 - 405 nm. A suitable source of excitation appears to be a source emitting radiation at this wavelength – 405 nm – in order for the radiation to be absorbed by the sample while emitting light of a different wavelength. A laser with a wavelength of 405 nm is used as a source based on the measured absorption spectra.

The L1 (Eu2O3) glass sample absorbs blue radiation with a wavelength of 405 mm and emits radiation in the spectrum range 600 nm to 640 nm. The relative value of luminescence reaches 71 relative units at the maximum. The L2 glass sample (Eu2O3, Tb2O3) absorbs blue radiation with a wavelength of 405 nm and emits radiation in the spectrum range 570 nm to 640 nm. The highest relative luminescence value reaches 91 relative units at the maximum. The L3 glass sample (Eu2O3, Sm2O3) absorbs radiation with a wavelength of 405 nm and emits radiation in the spectrum range 570 to 670 nm. Comparing the emission of glasses with different oxide content (Eu2O3, Tb2O3, Sm2O3), we conclude that the glass sample L2 (Eu2O3, Tb2O3) shows the most intense radiation emission of 91 relative units in the region of the spectrum 600-640 nm.

The absorption spectra and emission spectra were compared for the individual glass samples L1, L2 and L3. All samples absorb in the blue region of the spectrum and emit in the red region of the spectrum. The spectral shift of the wavelengths from the region 395 - 405 nm to the region usually 570 to 670 nm depends mainly on the chemical composition of the glass, especially on the content of Eu_2O_3, Tb_2O_3, Sm_2O_3. The L2 sample containing Eu_2O_3, Tb_2O_3 shows the most intensive absorption of 1.3 relative units and the emission of 90 relative units, while the lowest absorption of 0.76 relative units in the blue region and the lowest emission of 23.5 relative units in the red region are shown by the L3 sample containing Eu_2O_3, Tb_2O_3. The L1 sample containing europium oxide shows an absorption value of 0.88 relative units and an emission of 70 relative units, which ranks second in terms of the tested samples in the achieved emission intensity parameters in the red region of the spectrum.

Within the literature, one can find articles that dealt with a similar topic, whether it was the production of glasses containing lanthanide elements, or they investigated the mechanism of photosensitivity of glasses, or they measured luminescence. Several interesting articles dealing with this topic are described in the following paragraphs.

Zhang Xi-Jan and others produced luminosilicate glass samples doped with Eu_20_3 and Dy_2O_3 and measured excitation spectra, emission spectra and thermal luminescence spectra of samples prepared in different atmospheres. The sample doped with Eu^{2+} shows a luminescence peak at 462 nm. And the Eu^{2+} and Dy^{3+} co-doped sample shows a luminescence peak at 457 nm. Afterglow can last more than 12 hours [18].

Ren Linjiao et al. investigated the luminescence properties of Ce/Tb/Eu co-doped calcium borosilicate glass through excitation and emission spectra, fluorescence lifetime and colorimetric analysis. The results of the spectra show that the Eu^{3+} ion concentration quenching occurs when the Eu_2O_3 concentration varies from 0.75 mol % to 1.00 mol % and Ce^{3+}, Tb^{3+} and Eu^{2+} ions are all donors that can transfer energy to Eu^{3+}. They confirmed the influence of the Eu^{3+} concentration on the luminescence intensity. Calcium borosilicate glasses can be adjusted from cool white to warm white within the glass excitation by controlling the Eu_2O_3 concentration [19].

Masayuki Nogami and Yoshihiro Abe compared Eu^{3+} ion fluorescence spectra in glasses of the $Al_2O_3.SiO_2$ system prepared by a sol—gel process. It was concluded that the Eu^{3+} ion is preferentially coordinated with Al-O− bonds, where Al^{3+} ions constitute the AlO_6 octahedra [20].

6 Conclusion

Lanthanoid glasses - Eu_2O_3, Sm_2O_3, Tb_2O_3 are able to effectively absorb radiation in the blue region of the spectrum and emit radiation in the red region of the spectrum. The different composition of glasses is analyzed in this work in order to find the optimal composition and clarify the effect of individual compounds on the intensity of radiation emission. Glass

containing Eu_2O_3 and Tb_2O_3 showed the highest value of radiation absorption in the blue region of the spectrum and the highest intensity of radiation in the red region of the spectrum, which makes it an optimal material that can be used to modulate the wavelength of incoming radiation as a glass filter. The possible application of such radiation is wherever the phenomenon can be used from medicine, through photography to the automotive industry, in which LED and laser sources are widely used, while appropriate wavelength selection plays a major role in detection and other systems.

A suitable glass sample for converting blue radiation into the red region of the spectrum appears to be the L1 sample with Eu_2O_3, which exhibits emission intensity at the highest radiation wavelength. The highest emission intensity is shown by sample L2 with Eu_2O_3 and Tb_2O_3 at a wavelength slightly lower than that of sample L1.

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