UDC 666.1.022.4:66.093.2

LUMINESCENT GLASSES FOR TRANSFORMATION OF X-RAY EMISSION IN RADIATION INTROSCOPES

O.V. Kazmina, A.N. Abiyaka, Yu.A. Moskalev, A.A. Dits

Tomsk Polytechnic University
E-mail: kazmina@tpu.ru

Compositions of luminescent glasses for transformers of X-ray emission in radiation introscopes have been developed. Investigation of X-ray-luminescence of inorganic glasses activated by rare-earth element ions at excitation by X-ray radiation is carried out. The technique of measuring luminosity of transformer X-ray luminescence by using equipment of radiation introscopes is tested.

One of the most important applications of luminescence phenomenon remains the penetrating rays transformation into visible light. Starting from X-rays discovery and up to now, roentgenoluminescence is a basic process of radioactive images visualization in introscopy and defectoscopy.

At present, large quantity of luminescence materials used as detectors or emission transformers in wide range of energies is known, but not all of them may be used as X-ray emission transformers in introscopes. The quality of radiation transformers is determined to a large degree by properties of initial materials, which must meet the following demands [1]:

- high absorption of ionizing radiation working beam;
- high position resolution;
- luminescence spectrum consistency with spectral characteristic of CCD-matrix or introscope photodetector;
- technological capability of production of a transformer in the form of sufficiently great area screen.

Inorganic glass may be an X-rays transformer. Owing to its unique properties – transparency in the visible spectrum range, sufficient strength, resistance to environmental influence, flexible technological effectiveness, permitting of producing goods of different forms by considerably simple means, glass is widely used for production of various devices of structural components and measuring units [2].

In spite of all listed advantages of glass over other materials, X-ray emission transformers has not been put into production in Russia. Overseas roentgenoluminescente glasses are produced by American company «Collimated Holes, Inc.», but glass composition developed by this company is not given in technical literature [3].

The purpose of the given paper is to develop compositions of luminescent glasses suitable for production of X-rays emission screen transformers, applyed in industrial defecto- and introscopy.

Oxides of rare-earth elements (REE) are examined as activators of glasses roentgenoluminescence. Specific character of physicochemical REE oxides is connected with the peculiarities of their electron composition, uncompleted orbitals. At absorption of electromagnetic radiation unpaired electrons pass form ground state level to excited state level. Luminescence occurs as a result of excited electrons reverse transfer to more low-energy levels.

Fusible three-component glass of $PbO-B_2O_3-SiO_2$ system with high content of lead (to 40 mole %) was chosen as a matrix on initial stage of working. The interest to the glass of a mentioned system is attracted by the fact that lead-containing glasses possess high density, which is directly connected with glass capability to absorb X-rays, resistance to coloration under radiation effect, high optical transmission in visible part of spectrum, as well as low boiling temperature.

Batches were synthesized from reagents of «ch.pure» brand to decrease admixture negative influence on luminescent properties of glass. Boiling of lead-containing glasses, activated by 2 wt. % of REE oxides was carried out in 200 ml corundum bowls at temperature 1200 °C. Glass mass was molded into cast-iron forms with further annealing. The samples were prepared in the form of polished plates of 5mm thick.

Methods of measurement of various materials roentgenoluminescence brightness, known at present time, are based on general scheme, including radiation source, measured sample, detector of roentgenoluminescence luminous flux, coincided with measuring device.

X-ray units with energy of 20...200kV or isotope sources of γ-emission, such as ^{75}Se, ^{241}Am with γ-quanta energy of 20...300 keV are used as radiation source. It should be noted that in the latter case isotope sources with low activity – in the range to 100 quanta/sec are used for providing radiation safety.

According to radiation source intensity and roentgenoluminescence brightness different detectors – luminescence meters – are used. Thus, in the case of isotope sources application, photoelectric multiplier (PEM), working in counting mode, are used. Using X-ray units, samples glow brightness is measured by PEM in current mode or selenium photocells in complex with galvanometer.

It should be noted that mentioned schemes are not accurate enough for brightness measurements. In the case of isotope sources – low statistic of γ-quanta limits measurement accuracy within 20 %. For X-ray units with PEM and selenium photocells application – instability of power packs working also limits measurements accuracy and results recurrence.

Besides, for determination of luminescent glasses fitness as introscope emission transformers, spectral compatibility of luminescence spectra of examined glass (maximal wave length of roentgenoluminescence spectrum is 500nm) and spectral sensitivity range of introscope CCD-matrices should be taken into consideration. In this connection ISD-017 AP CCD camera of RIN-120 introscope with matrix working in the mode of light signal accumulation was used as measuring device. X-ray unit RUP-150/300V was used as a radiation source. Scheme of measuring is presented in fig. 1.

In the given measurement procedure the issue of spectral correspondence of glasses roentgenoluminescence and CCD-matrix sensitivity was automatically decided. Due to signal accumulation at the matrix, measurements accuracy increases. Using software «Diada» several glasses samples were simultaneously measured and their brightness was compared with etalon.

All measurements were carried out at two modes of X-ray unit – 100 kV/3 мA and 220 kV/6 мA. X-ray filter – 1,5 mm steel plate was used for extracting radiation soft component (less than 50 keV).

Measurements for glasses with different activators were carried out for determining optimal components ratio and activators concentration (table 1). It was stated that glass activated with terbium had maximal glow intensity, therefore further investigations were carried out using this activator.

To determine the influence of terbium oxide concentration on glow intensity, its quantity in glass was changed in the range from 2 to 15 wt. %. Measurements, carried out at accelerating voltage 220 kV and current 6mA, allows us to determine the dependence of glow intensity increase from 300 to 750 arbitrary units on activator concentration (fig. 2). It is clear that dependence straight portion after 10 wt. % of Tb_4O_7 and insignificant decrease of glow intensity is connected with concentration quenching effect. 10 wt. % of terbium oxide is chosen as an optimal quantity of activator.

In spite of comparatively easy glass formation of lead-containing compositions, obtaining glass of this system with specified properties is connected with certain difficulties, such as high nonhomogeneity of glass mass, liquation presence. One of the reasons of nonhomogeneity is high volatility (to 14 wt. %) from the surface of glass mass mirror of plumbic ochre. Two and more phases liquation decomposition of a melt for glasses of investigated system $PbO\text{-}B_2O_3\text{-}SiO_2$, may be latent if plumbic ochre content is higher than 20 wt. %, that finally complicates the production process of specific structure glass. Moreover, red lead (Pb_3O_4), by means of which plumbic ochre is added to glass, belongs to hazardous substance of the 1 category.

Table 1. *Glow intensity of lead glasses, activated by 2wt. % of REE*

Activator	Accelerating voltage, kV	Current, мA	Intensity of glow, arbitrary unit
CeO_2	100 220	3 6	20 60
Nd_2O_3	100 220	3 6	20 30
Sm_2O_3	100 220	3 6	35 100
Eu_2O_3	100 220	3 6	30 120
Gd_2O_3	100 220	3 6	30 60
Tb_4O_7	100 220	3 6	50 300
Dy_2O_3	100 220	3 6	40 200
Ho_2O_3	100 220	3 6	20 40
Yb_2O_3	100 220	3 6	30 60

Taking into consideration the facts stated above, and essentially in connection with low characteristics of lead-containing glass luminosity scintillating glasses compositions of $Li_2O\text{-}BaO\text{-}SiO_2$ and $Al_2O_3\text{-}B_2O_3\text{-}SiO_2$ systems were examined as basic matrices (table 2). Technical scintillation efficiency of these glasses, activated with cerium oxide, at excitation by γ-rays, according to the data of paper [4], is 2...3 wt. % relative to NaI (Tl) crystal.

As it was mentioned before, the results of glow intensity of lead-containing glasses were obtained at the samples with a preliminary prepared surface, which was

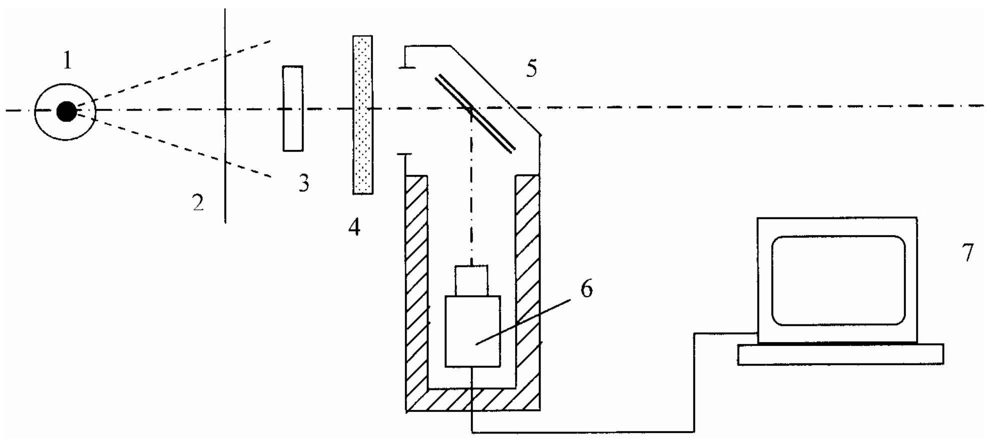

Fig. 1. *Scheme of roentgenoluminescence brightness measurement: 1) radiation source is X-ray unit; 2) X-ray emission filter; 3) the observable sample of luminescent glass; 4) protective glass; 5) X-ray sensitive block of introscope; 6) CCD-matrix; 7) computer*

treated by means of polishing process. While polishing, favorable conditions for leaching, developing in glass coating surface, contacting with water are created. The result of this process is sodium ions yield from a thin near-surface layer of glass. At growth of irritative quanta energy increasingly more part of light is absorbed in a leached layer, not containing luminescence. Further comparative analysis of different compositions glasses was realized on glasses powders to remove influence of sample surface quality on its brightness measurements results.

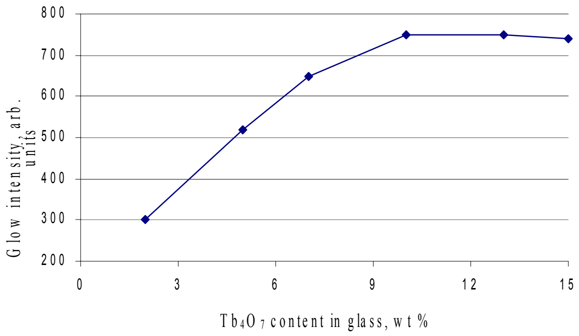

Fig. 2. *Dependence of lead-containing glasses glow intensity on Tb_4O_7 concentration*

Table 2. *Compositions of glasses with 10 wt. % of Tb_4O_7 content*

Glass code	Glass composition, wt. %							Additional admixtures, more than 100 %			
	B_2O_3	SiO_2	Li_2O	BaO	MgO	Al_2O_3	Na_2O	WO_3	NH_4F	C	GdO
1	7,29	64,81	9,68	18,21	–	–	–	–	2	–	–
2	7,29	64,81	9,68	18,21	–	–	–	–	–	2	–
3	7,29	64,81	9,68	14,57	3,64	–	–	–	2	–	–
4	7,29	64,81	9,68	18,21	–	–	–	20	–	–	–
5	7,29	64,81	9,68	14,57	3,64	–	–	–	–	–	–
6	7,29	64,81	9,68	14,57	3,64	–	–	–	–	–	5
7	34,08	39,17	–	–	–	16,64	10,11	–	–	–	–
8	34,08	39,17	–	–	–	16,64	10,11	–	–	–	5

Synthesis of glasses activated with 10 % of terbium oxide was realized in corundum bowls at temperature 1350 °C, with further annealing in a bowl, glass comminuting and 0,315...0,15 mm fraction extraction.

Glass (№ 1, table 2), conforming to 3-56-8 type has been chosen as initial composition. Terbium may exist in glass mass in tri- and tetravalent forms, between which Tb^{3+}/Tb^{4+} equilibrium, determined by composition and synthesis temperature conditions is ascertained. Taking into account the fact that only ion Tb^{3+} has a capacity to luminesce, carbon was additionally introduced into glass composition for creation of boiling reducing conditions, to shift the reaction to the side of trivalent terbium formation (№ 2, table 2). To increase glass density and correspondingly its absorptive capacity, heavy element in the form of tungsten oxide was additionally introduced into glass base composition (№ 4, table 2). Besides, glass compositions with partial substitution of baryta to magnesium oxide were tested (№ 3, 5). The results of investigation of researched compositions glow intensity are presented in fig. 3.

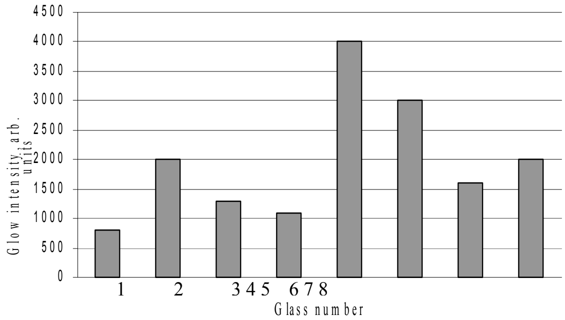

Fig. 3. *Glow intensity of glass powders of various composition (120 kV, 3 mA, exposition 4 s)*

As it is seen from obtained data (fig. 3) that glow intensity of base composition glass powder increases in the case of carbon to 2000 arbitrary units using. Tungsten oxide introduction into glass composition insignificantly increases glow intensity to 1100 arbitrary units, in comparison with 800 arbitrary units of base composition (№ 1).

Composition with 20 % substitution of baryta to magnesium oxide has peak luminosity (4000 arbitrary units). The growth effect of glass luminescence with magnesium is also noted in paper [5], where it is sated that partial substitution of baryta cation for magnesium oxide (5...10 mole %) promotes increase of relative scintillation efficiency of alkali-free fluorine-containing glasses. Moreover, roentgenoluminescence yield of composition with magnesium and fluoric ammonium (№ 3) is insignificant, just 1300 arbitrary units.

Data of REEs interaction influence on material luminescent characteristics are known. At comparatively low concentrations the interaction is mostly expressed in energy transfer from one REE to another, hereupon quenching of one or both interacting ions, suppression of one REE and sensitization of it by another or only sensitization of another may be observed. At high concentrations another features of interaction may be observed: absorption and luminescence spectra changing. In paper [6] experimental data of sensitizing influence of dysprosium, cerium and gadolinium on terbium in inorganic glass are presented, therefore, composition with 5 % gadolinium oxide introduction was additionally tested (№ 7). In this case glow intensity was 3000 arbitrary units, that is higher in comparison with base composition, but lower than maximal luminous compound with barium to magnesium changing (№ 5).

Thus, glass roentgenoluminescence intensity depends not only on activator type and its concentration, but also on base glass composition, changing which by additional modifiers interacting, luminescence yield may be increased.

Using glass as X-rays transformer, its technological characteristics should be taken into consideration, some of them may be predicted, taking into account the diagram of system status, which the given composition is referred to. Specifically, initial glass composition of Li_2O-BaO-SiO_2 system (a dot in a diagram of fig. 4), unlike lead-containing glasses, does not have metastable liquation and possesses low tendency to crystallization, that is conditioned by low melting temperature (approximately 950 °C) and composition staying in eutectic points area.

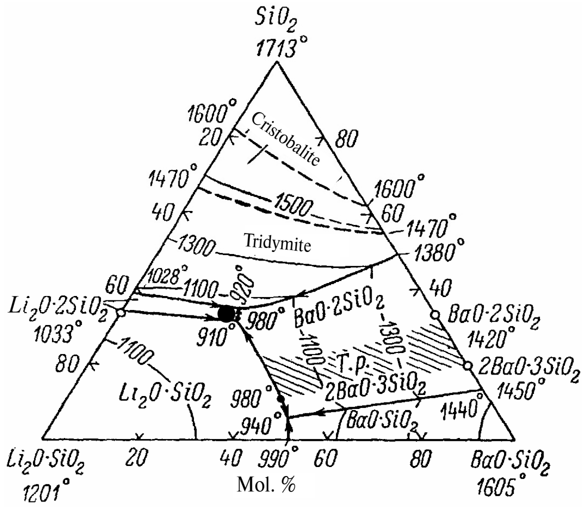

Fig. 4. *Diagram of system $Li_2O{\cdot}SiO_2$-$BaO{\cdot}SiO_2$ status*

According to scientific data, glass 1,0Na_2O·0,3Ce_2O_3*(3...4) B_2O_3, SiO_2*(1,0...1,3) Al_2O_3 [7] is recommended as a material efficiently scintillating under γ-radiations influence, using activator-cerium oxide. The given composition, recalculated for terbium oxide, was chosen as a base one (№ 7, table 3) with additional introduction of the second REE – GdO (№ 8). By quantity of glass formers – silicon and boron oxides, glass mass is distinguished by high resistance to glass formation. Maximal temperature of boiling process made 1350 °C, with further annealing at 500 °C.

Glow intensity of obtained glass powders made 1600 and 2000 arbitrary units for compositions (№ 7, 8) respectively. Presence of gadolinium oxide at a rate of 5 % in glass composition rather increases luminescence outflow. Obviously, in the case of gadolinium and terbium simultaneous presence in glass system Al_2O_3-B_2O_3-SiO_2 there is energy transfer at which activator sensitization occurs.

As it is seen from diagram of status (fig. 5), the investigated glass composition is in mullite $3Al_2O_3{\cdot}2SiO_2$ crystallization area, close to boundary line, that corresponds to its comparatively low tendency to crystallization. Presence of sodium oxide in glass composition decreases melting temperature and crystallization capacity. But the given glasses compositions possess smaller luminescence outflow in comparison with glasses of Li_2O-BaO-SiO_2 system.

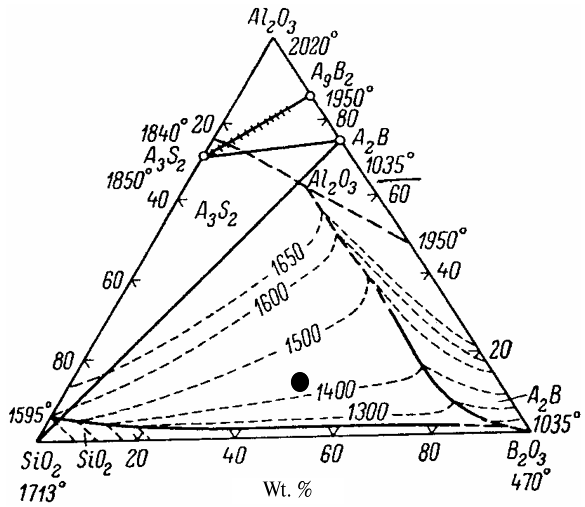

Fig 5. *Diagram of status Al_2O_3-B_2O_3-SiO_2*

Thus, on the ground of scientific data analysis and obtained results it follows that inorganic glass of developed compositions may be used as introscopes X-rays transformer owing to transparency in the visible spectrum range, sufficient strength, flexible processibility and high specific light yield.

The work is performed with support of departmental scientific program of Ministry of Education of RF»Development of high school scientific potential» in the area «New materials and chemical technologies, including nanomaterials and nanotechnologies».

REFERENCES

1. Devices for nondestructive testing of materials and goods. V. 1 / Ed. by V.V. Kluev. – 2-nd issue revised and added. – Moscow: Mashinostroenie, 1986. – 488 p.
2. Byurganovskaya G.V., Vargin V.V., Leko N.A., Orlov N.F. Influence of emissions on inorganic glasses. – Moscow: Atomizdat, 1968. – 244 p.
3. http://www.collimatedholes.com/
4. Glass. Reference book / Edited by N.M. Pavlushkin. – Moscow: Stroiyizdat, 1972. – 487 p.
5. Optical and spectral properties of glasses: Theses of VI National Symposium on optical and spectral properties of glasses. – Riga: P. Stuchki's LSU, 1986. – 210 p.
6. Karyakin A.V., Anikina L.I., Pavlenko L.I., Laktionova N.V. Spectrum analysis of rare-earth oxides. – Moscow: Nauka, 1974. – 154 p.
7. Reference book on glass production / Edited by I.I. Kitaygorodskiy. – Moscow: Gosstroyizdat, 1963. – V. 1. – 1026 p.

Arrived on 30.03.2006