Synthesis and properties study of the X-ray phosphors Gd$_2$O$_2$S:Tb

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Abstract. Gd$_2$O$_2$S:Tb based X-ray stimulated luminescent phosphors for X-ray intensifying screens, X-ray-visible light converters and bio-imaging are synthesized using two different methods (in a neutral or reducing atmospheres). The effects of atmosphere at synthesis, activator and flux content in the charge mixture and crucible lacing upon the prepared phosphors phase composition and luminescence intensity are studied. The optimal synthesis conditions are determined affording a Gd$_2$O$_2$S:Tb phosphor free of admixture phases and providing the highest luminescence intensity upon excitation with «hard» X-ray irradiation. The synthesized phosphor is characterized by particle size distribution analysis and X-ray stimulated luminescence spectra measurements.

1. Introduction
The X-ray phosphors are widely used in such branches of industry as medicine, non-destructive testing and bioimaging [1-3]. Nowadays terbium activated gadolinium oxysulphide (Gd$_2$O$_2$S:Tb) is one of the most effective X-ray phosphors [4]. Its high intensity of the luminescence having its maximum in the «green» spectral range allows using the green emitting intensifying screens of this phosphor for decreasing the exposure of the roentgenographic images that reduces the irradiation of the patients and medical staff. Inasmuch the insignificant intensity rising causes the strong reduction of the exposure this makes it important to synthesize the Gd$_2$O$_2$S:Tb phosphors with high intensity. However luminous intensity of such phosphors commercially fabricated by different manufacturers can vary in a wide range. This is because even the very small amount of the impurities imported into the phosphor from the atmosphere or from the crucible during the synthesis, would reduce the luminescence efficiency [5].

So it is very important to study how the different synthesis techniques affect the intensity of the X-ray luminescence.

2. Experimental
Gd$_2$O$_2$S:Tb phosphors were synthesized by the high-temperature annealing of the batch-mix with the impurities afterwashing. The raw materials for the synthesis were the gadolinium and terbium oxides (Gd$_2$O$_3$ and Tb$_2$O$_3$). The assay percentage in the oxides were 99.999 %. To prepare the oxysulfides from the oxides we put into the batch-mix the sulfo-mix made-up of sulfur and anhydrous sodium carbonate. Sulfur was added into the batch-mix in amounts from 8.6 to 15.0 wt%. The amount of the terbium oxide was calculated as 0.13 - 9.0 wt% of terbium in the finished phosphor. Beyond that, the LiF and Na$_4$P$_2$O$_7$ were added into the batch-mix as a flux agents.
During the process of the batch-mix annealing the several reactions have place [6]. At the temperature of 270…350 °C sodium carbonate reacts with sulfur and it’s a polysulphide Na$_x$S reaction, where $x=1…5$:

\[
\text{Na}_2\text{CO}_3 + \text{S} \rightarrow \text{Na}_2\text{S} + \text{Na}_2\text{S}_x + \text{SO}_2 + \text{CO}_2. \tag{1}
\]

Then at the temperature of 400…950 °C melted polysulphides reacts with gadolinium and terbium oxides with formation of the oxisulphides:

\[
\text{Gd}_2\text{O}_3 + \text{Na}_2\text{S}_x \rightarrow \text{Gd}_2\text{O}_2\text{S} + \text{flux} + \text{SO}_2. \tag{2}
\]

In our work the x-ray phosphors were synthesized by two different methods: in the neutral atmosphere [7] and in the reducing atmosphere [8].

At synthesis in the neutral atmosphere batch-mix was baked in a corundum crucible in nitrogen flow in the tube furnace. In is the traditional method of synthesis using for commercial manufacturing of phosphors. At synthesis in the reducing atmosphere batch-mix was baked in a corundum crucible under the active carbon pillow. The reducing atmosphere was created by the carbon monoxide CO forming as a reaction of active carbon and oxygen in the batch-mix.

Heat treatment conditions at synthesis were held as follows: heating from the room temperature to 1130 °C in 6 hours; holding at 1130 °C for 2 hours; then cooling in the oven. Such a long heating time was necessary for the uniform heating across the whole width of the batch-mix, due to its poor thermal conductivity. In some cases to prevent the contact of the batch-mix with the crucible walls, the aquadag coating was used. Crucible was coated with the water suspension of highly dispersed mineral carbon and surface active agents. After drying of the aquadag mineral carbon formed the protective layer on the crucible walls.

On completing of the synthesis the phosphor was washed from the polysulphides firstly with the bidistilled water, then with the 5% chlorine hydride solution and finally again with the bidistilled water up to the neutral pH. Washed phosphor was dried at 120 °C and riddled through the 71 μm size.

X-ray spectra of the synthesized phosphors were studied with AvaSpec-3648 fiber optic spectrometer (Avantes, Netherlands). X-ray emission was exited with the X-ray generator RPD-200 (Syntez NDT, Russia) at the 100 kV tungsten anode voltage and at 2 mA current rate. Intensity of the X-ray luminescence was counted as a surface area under the spectra curve. X-ray phase analysis of the synthesized phosphors was made with the X-ray diffractometer Rigaku SmartLab 3 (Rigaku Corporation, Japan). The dispersiveness study was carried out by the scanning electron microscope Tescan VEGA 3 SBH (Tescan, Czech Republic) with further analysis of the microphotographs with the «ImageJ» software suite.

3. Result and Discussion

Figure 1 represents the X-ray diffraction pattern of the phosphors synthesized in the neutral atmosphere. You can see that the unwashed phosphor include the sodium polysulphides impurities - Na$_2$S$_3$ and Na$_2$S$_5$. Sodium polysulphides impurities were removed at washing, hence the phases of the gadolinium aluminates GdAl$_{11}$O$_{18}$ and GdAlO$_3$ are present in the phosphors being synthesized in the crucible without the carbon protective layer. The cause of aluminate phases forming is the aluminum from the corundum crucible walls. As was already mentioned, to prevent this effect we covered the crucible walls with the protective layer. X-ray diffraction pattern of the phosphor synthesized in the crucible with the carbon protective layer is also given at figure 1.

One can see that aluminate phases are absent but rather than gadolinium oxisulphide (Gd$_2$O$_2$S) we have the mix of the gadolinium sulphide (GdS) and terbium sulphide (TbS) phases. It appears that the carbon protective layer helps the reduction of gadolinium and terbium from Gd$^{3+}$ and Tb$^{3+}$ to Gd$^{2+}$ and Tb$^{2+}$ respectively. Therefore synthesis in the neutral atmosphere does not allow getting the required phase content of the phosphor.
Figure 1. X-ray diffraction patterns of the phosphors synthesized in the neutral atmosphere:
(a) - crucible with the carbon layer, sulphur content 15.0 wt%, before washing;
(b) - crucible without the carbon layer, sulphur content 15.0 wt%, after washing;
(c) - crucible without the carbon layer, sulphur content 8.6 wt%, after washing;
(d) - crucible with the carbon layer, sulphur content 15.0 wt%, after washing.

Figure 2 shows the X-ray diffraction patterns of the phosphors synthesized in the reducing atmosphere with different content of terbium. In this case one can see that all peaks of all phosphors are congruent to gadolinium oxysulphide Gd$_2$O$_2$S (PDF card 26-1422). Impurities phases peaks are absent on the diffraction patterns. So, synthesis in the reducing atmosphere allows getting the phosphor with the required phase content without any impurity phases.

Although all the peaks of all phosphors being synthesized in the reducing atmosphere are congruent to the hexagonal configuration of Gd$_2$O$_2$S, the intensities of the peaks are significantly different. According to the relative intensity of the peaks, phosphor with the minimum content of terbium (0.13 wt%) is mostly congruent to the PDF card 26-1422. As terbium concentration grows, we can see the increasing intensity of the peaks (100) at the angle of 2$\theta$ = 26.73° and (003) at the angle of 2$\theta$ = 40.58°. Though, at the angle of 2$\theta$ = 29.94° and at the angle of 2$\theta$ = 38.13° intensity of the peaks 101 and 102 (respectively) is falling. As may be supposed, terbium injection into the phosphor structure causes forming of the polytypes of cubic packing layers in the hexagonal structure of Gd$_2$O$_2$S lattice.

Despite the fact that the phase content of the phosphors differ widely from each other, location of all x-ray spectral bands are congruent. The only difference is intensity. So as an example on the figure...
3 is represented the x-ray spectra of the phosphor synthesized in the reducing atmosphere with the 10 wt% of sulfur content in the batch-mix and 0.13 wt% of terbium content. The most intensive spectral band is located in the «green» spectral zone and has its maximum at 544 nm. This band is congruent to the transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$ in the Tb$^{3+}$ ion [9].

Figure 2. X-ray diffraction patterns of the phosphors synthesized in the reducing atmosphere with different concentration of terbium: (a) – 9.0 wt% Tb; (b) – 2.0 wt% Tb; (c) – 1.0 wt% Tb; (d) – 0.5 wt% Tb; (e) – 0.13 wt% Tb; (f) - Gd$_2$O$_2$S (PDF card 26-1422).
Figure 3. X-ray luminescent spectrum of synthesized Gd$_2$O$_2$S:Tb phosphor

Intensities of the x-ray luminescence was counted from the surface area under the spectra curves of the synthesized phosphors. Table 1 gives the comparison of the relative intensities of the x-ray luminescence. The intensity of the commercial phosphor Gd$_2$O$_2$S:Tb KEP-545 («RPF «Luminofor» Corp.», Russia) is also given for reference.

Table 1. Comparing of the x-ray luminescence intensities of the synthesized phosphors.

| Sample number | Atmosphere of the synthesis | Carbon layer of the crucible | Elements concentration, wt% | Relative intensity, % |
|---------------|-----------------------------|------------------------------|-----------------------------|----------------------|
|               |                             |                              | Tb | S | Na$_2$P$_2$O$_7$ | |
| 1             | Neutral                     | yes                          | 9.0 | 15.0 | | 9.6 |
| 2             |                             |                               | 9.0 | 15.0 | | 37.2 |
| 3             |                             |                               | 9.0 | 8.6  | | 7.4 |
| 4             | Reducing                    | no                            | 9.0 | 15.0 | absent | 40.2 |
| 5             |                             |                               | 9.0 | 8.6  | | 60.0 |
| 6             |                             |                               | 0.5 | 10.0 | | 74.7 |
| 7             |                             |                               | 1.0 | 10.0 | | 75.0 |
| 8             |                             |                               | 2.0 | 10.0 | | 75.6 |
| 9             |                             |                               | 0.13 | 10.0 | 8.0 | 142.7 |
|               | Commercial phosphor KEP-545 |                              | | | | 100.0 |

It is apparent that phosphors synthesized in the reducing atmosphere are more intensive that phosphors synthesized in the neutral atmosphere. Presumably it is because they do not have any impurity phases in their content, which could reduce the intensity (as it have been shown on the diffraction patterns given above). Using the carbon protective layer of the crucible leads to decrease of
the x-ray luminescence intensity. As may be supposed it is conditional upon the changes in the phase content of the phosphor. The impact of the sulfur content in the batch-mix on the intensity of the x-ray luminescence is rather complex. The maximum intensity of the phosphors synthesized in the neutral atmosphere is observed at 15.0 wt% of sulfur in the batch-mix. For the phosphors synthesized in the reducing atmosphere the maximum of the intensity is observed at 8.6 and 10.0 wt% of sulfur in the batch-mix. We can suppose that during the synthesis in the reducing atmosphere forming of the oxysulphide from the gadolinium oxide goes not by the reaction (2) but by the following reaction:

$$\text{Gd}_2\text{O}_3 + \text{Na}_2\text{S}_x + \text{CO} \rightarrow \text{Gd}_2\text{O}_2\text{S} + \text{flux} + \text{CO}_2.$$  \hspace{1cm} (3)

In that case the gaseous volatile co-product of the reaction would be not the sulphur dioxide but the carbon dioxide. It reduces the reaction losses of sulfur at phosphor synthesis and allows to inject the less content of sulfur into the batch-mix than at synthesis in the neutral atmosphere.

The most significantly growth of the x-ray luminescence is observed at injecting the sodium pyrophosphate (Na$_4$P$_2$O$_7$) into the batch-mix. Phosphor synthesized using the Na$_4$P$_2$O$_7$ as fluxing agent has the higher intensity of the luminescence than commercial phosphor of the analogous content KEP-545. To explain it, look at the figure 4 that represent the scanning electron microphotographs of the phosphors synthesized with (b) and without (a) the sodium pyrophosphate. It’s evident that Na$_4$P$_2$O$_7$ injection into the batch-mix increases the particles size of the phosphor from 1.6 to 9.9 μm. The more coarst phosphor has the less surface area of grains and consequently contains the less number of the surface nonradiative recombination centers that decreases the yield if the x-ray luminescence.

Though we can say that phosphor synthesized in the reducing atmosphere with injection of the sodium pyrophosphate has the highest intensity of the X-ray luminescence of all synthesized phosphors. The average grain size of this phosphor is 9.9 μm. Such dispersity allows getting the roentgenograms of rather high definition when using this phosphor in the X-ray intensifying screens.

**Figure 4.** SEM images of synthesized phosphors: (a) - without Na$_4$P$_2$O$_7$ flux; (b) - with Na$_4$P$_2$O$_7$ flux.

### 4. Conclusions

As a result of our studies it have been found that synthesizing Gd$_2$O$_2$S:Tb phosphors in the reducing atmosphere with injection of the Na$_4$P$_2$O$_7$ fluxing agent into the batch-mix allows to increase significantly the intensity of the x-ray luminescence in compare with the traditionally synthesized commercial phosphors. Increasing of the x-ray luminescence intensity is caused by getting the
phosphor of high dispersity and without any impurity phases. As well, this method of synthesis is more technologically simple and cost-effective that traditional synthesis in the neutral atmosphere and it doesn’t require any tube furnace and nitrogen. And in fact it allows to reduce the sulfur consumption and abate the SO$_2$ air emissions. Using the developed technology the phosphor 1.4 times effective in the intensity of the X-ray luminescence then commercial KEP-545 of the analogous content was synthesized.

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