

# Luminescent properties of $\text{Ba}_x\text{Mg}_{(2-x)}\text{F}_4:\text{W}$ ceramics

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DOI: 10.32523/ejpfm.2023070103

Received: 16.02.2023 - after revision

Ceramics based on alkaline earth metal fluorides activated by tungsten has been obtained by radiation synthesis. The synthesis was realized by direct action on the mixture with an activator of a powerful flow of high-energy electrons without the use of any additives to facilitate the synthesis. It has been established that the resulting ceramics have luminescent properties characteristic of tungsten-activated materials based on metal fluorides.

**Keywords:** alkaline earth metal fluorides; tungsten; radiation synthesis; photoluminescence

## Introduction

The registration of high-energy radiation flows is carried out by converting radiation energy into luminescence using scintillation materials. Fluorides of alkali and alkaline earth metals doped with polyvalent ions are the promising scintillators. However, the introduction of dopants into the crystal lattice is a difficult task. So, fluorides such as  $\text{LiF}$ ,  $\text{MgF}_2$ ,  $\text{BaF}_2$ , are characterized by high structural perfection. Dopants – polyvalent ions, replacing lattice cations metal, are difficult to integrate into the lattice due to the difference their charges

and sizes in compare to that for lattice cations [1]. Therefore, to embed dopant ions in lattice, it is necessary to introduce additional elements into materials to compensate for these differences. For example, synthesis from LiF (NaF) and  $YF_3$  ( $GdF_4$ ), having cubic and rhombic lattices, leads to the formation of materials in which the presence of internal lattice distortions facilitated the introduction of a dopant [2–7].

A possible option for a heavily doped scintillating material is  $BaMgF_4$ , obtained from  $BaF_2$  and  $MgF_2$ , which have a fluorite and rutile lattice, respectively. W, U ions are effective dopants in materials based on metal fluorides. However, their introduction into the crystal lattice is difficult. Due to high temperatures hexafluoride compound of these dopants, having low melting temperatures (for  $WF_6$  and  $UF_6$  are 2.3 and 64 °C, respectively), removed from the melt during the crystal growth.

A promising method for obtaining doped scintillators from refractory materials under radiation beam was demonstrated in [8, 9]. Radiation synthesis was carried out only at the expense of radiation energy, only from charge materials of stoichiometric composition for a time less than 1 s, in air. It can be expected that tungsten ions will not have time to leave the zone in which ceramics are formed during the radiation synthesis and will enter the lattice. To facilitate the introduction of W ions into the mixture, lithium hydroxide was added.

The purpose of this work is to experimentally test the possibility of radiation synthesis of ceramics based on  $BaF_2$  and  $MgF_2$  without addition of any materials that promote synthesis, and researches of an optical property of as-synthesized  $BaF_2$ ,  $MgF_2$  and  $BaMgF_4$  ceramics samples and these materials doped with tungsten trioxide as well.

## Synthesis of ceramics

For the synthesis, industrial high-purity powders of Ba and Mg fluorides were used. The dopant was added to the charge in the form of  $WO_3$  powder in an amount of 2–3% of the total weight. The bulk densities of the charges were (1.43–1.49), (0.64–0.71), and (1.38–1.45) g/cm<sup>3</sup> for synthesis of  $BaF_2$ ,  $MgF_2$ , and  $BaMgF_4$ , respectively. The composition of the charge for the synthesis of  $BaMgF_4$  was 73.8%  $BaF_2$  and 26.2%  $MgF_2$ .

A charge with a volume of 35 cm<sup>3</sup> was poured into the cavity of 0.7 cm deep in a massive copper crucible with dimensions of 110 × 50 × 40 mm<sup>3</sup>. The synthesis was carried out by direct exposure of the charge to a flow of 1.4 MeV electrons and a power density of 18 kW/cm<sup>2</sup> from the ELV-6 accelerator. An electron beam having Gaussian space distribution and a cross section of 0.5 cm<sup>2</sup> at half height had been scanning over the charge surface at a frequency of 50 Hz. The crucible moved at a speed of 1 cm/s in the plane perpendicular to the scanning plane. The total time of irradiation of the charge in the crucible was 10 s.

As-synthesized ceramics samples are shown in Figure 1. The  $BaF_2$  ceramic was formed in the form a plate with the surface about half the area of the crucible

base and an average thickness of 5 mm. As for  $\text{MgF}_2$ ,  $\text{BaMgF}_4$  ceramics samples, they had irregular oval shapes from 35 to 5 mm<sup>2</sup> in size. Thickness of the samples reached 5 mm.

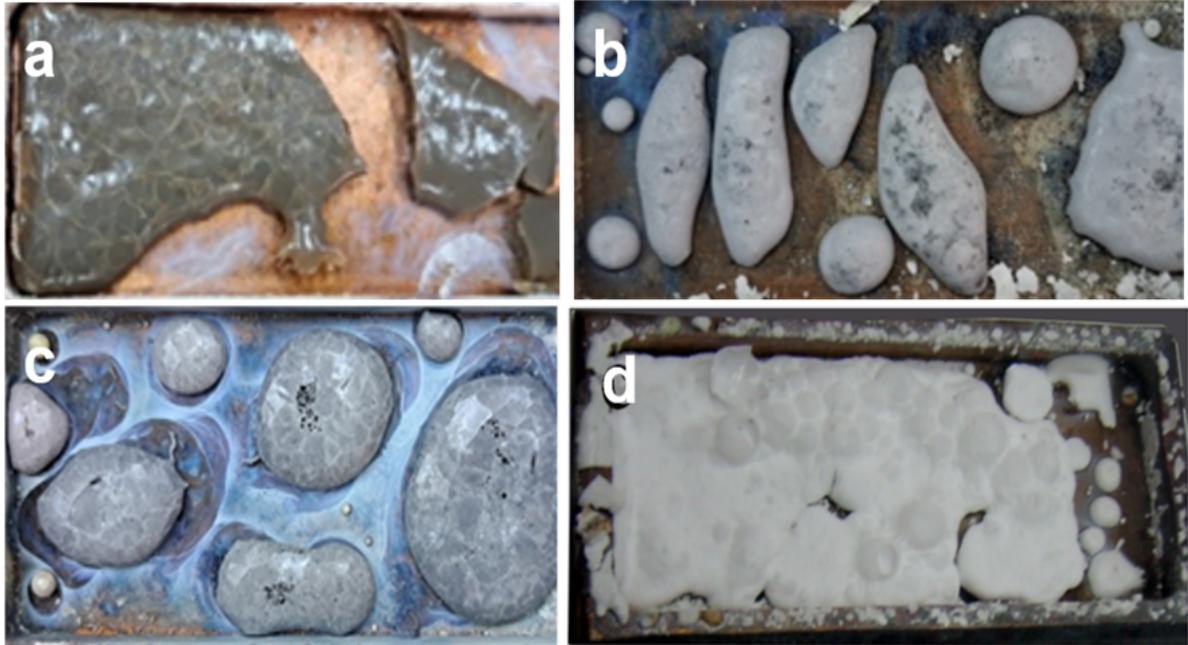


Figure 1. View of as-synthesized samples in crucibles:  $\text{BaF}_2$  (a),  $\text{MgF}_2$  (b) and  $\text{BaMgF}_4:\text{W}$  (c),  $\text{Ba}_{0.5}\text{Mg}_{1.5}\text{F}_4$  (d)

## Photoluminescence of ceramics samples

To measure photoluminescence (PL), ceramic samples were ground. The PL and excitation spectra of the PL were measured using a CM2203 SOLAR spectrometer. All measurements were performed under equal conditions; the powders for measurements were poured into identical cuvettes.

The results of studying the PL of  $\text{BaF}_2$  samples with different dopant content are shown in Figure 2. For each material, a series of measurements of PL spectra were carried out.

PL spectra consist of the band with maximum at 500 nm and FWHM equal to 0.9 eV in samples different series. There is a certain scatter in the value of the luminescence intensity in the samples of the same series. However, the tendency to increase in PL intensity with an increase in the content of tungsten trioxide in the charge is quite obvious. In samples of  $\text{BaF}_2$  ceramics containing 2 or 3% tungsten trioxide in the charge, the PL intensity at 500 nm is 10 or 18 times higher than in undoped samples, respectively. This means that W can be introduced into the lattice during radiation synthesis.

Note that the excitation spectra of PL at 500 nm, shown in Figure 2, insert, depend on dopant content. With the increasing of the dopant in the charge the intensity ratio between bands at 250 and 220 nm changes from 0.6 till 2.5 only due to the growth of the band at 250 nm.

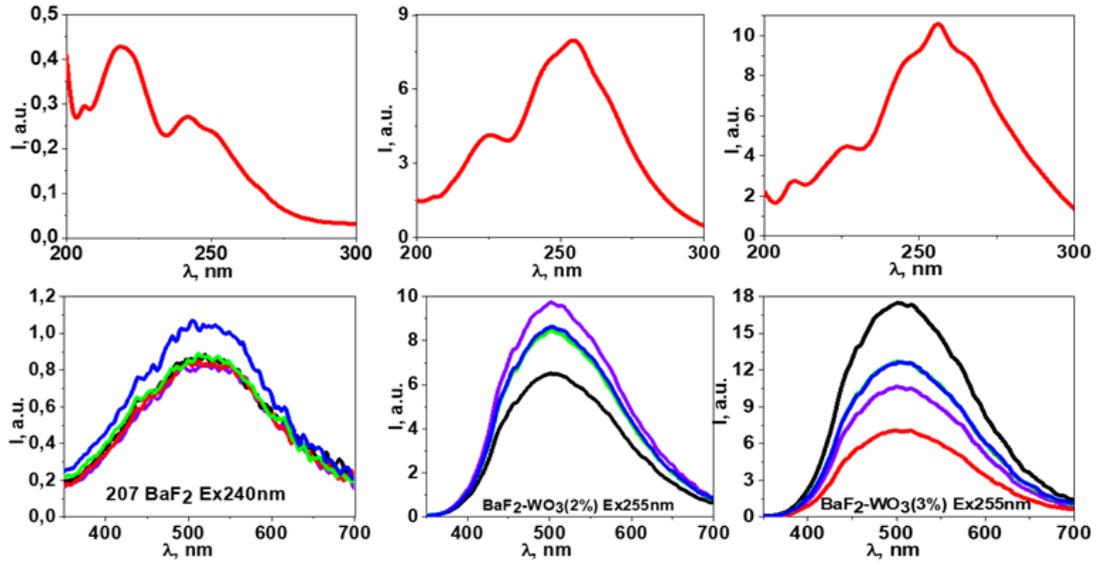


Figure 2. PL spectra of  $\text{BaF}_2$  ceramic samples doped with tungsten trioxide. Inserts: excitation spectra of the PL emission

The results of studying the PL of  $\text{MgF}_2$  and  $\text{BaMgF}_4$  ceramic samples are presented in the Figure 3 and Figure 4.

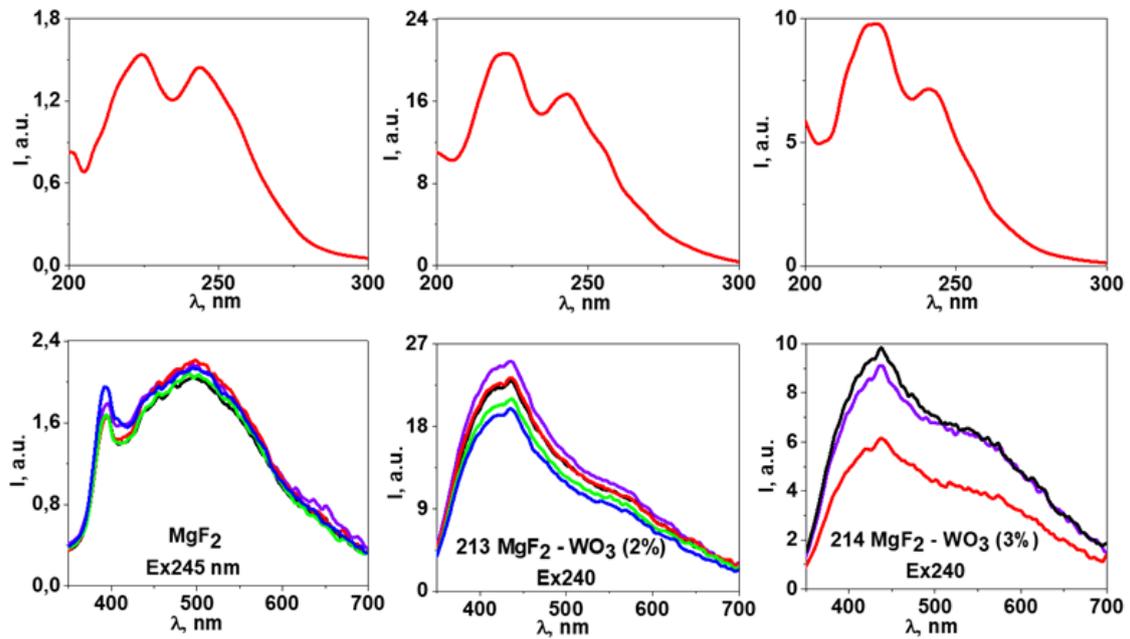


Figure 3. PL spectra of  $\text{MgF}_2$  ceramic samples doped with tungsten trioxide. Inserts: excitation spectra of the PL emission

The PL spectra of  $\text{MgF}_2$  ceramic samples differ from those measured in  $\text{BaF}_2$ . The PL spectra in  $\text{MgF}_2$  ceramics consist of the bands in region 440 and 600 nm with the FWHM values of 0.85 and 0.3 eV, respectively. The presence of the  $\text{WO}_3$  dopant leads to increase both the intensity of the bands and the relative contribution of the band at 600 nm.

The PL excitation spectra in  $\text{BaF}_2$  and in  $\text{MgF}_2$  ceramic samples are similar and consist of two bands at 220 and 250 nm. In contrast to ceramics based on

$\text{BaF}_2$ , the band at 220 nm in excitation spectra of  $\text{MgF}_2$  samples dominates. The introduction of the tungsten trioxide leads to increase not only the intensity of the bands but also the relative contribution of the band at 220 nm.

The luminescence spectra of ceramic  $\text{BaMgF}_4$  samples doped with  $\text{WO}_3$  shown in Figure 4, similar to the PL spectra in doped  $\text{BaF}_2$  samples ceramics and consist of an emission band with a maximum in the region of 500 nm.

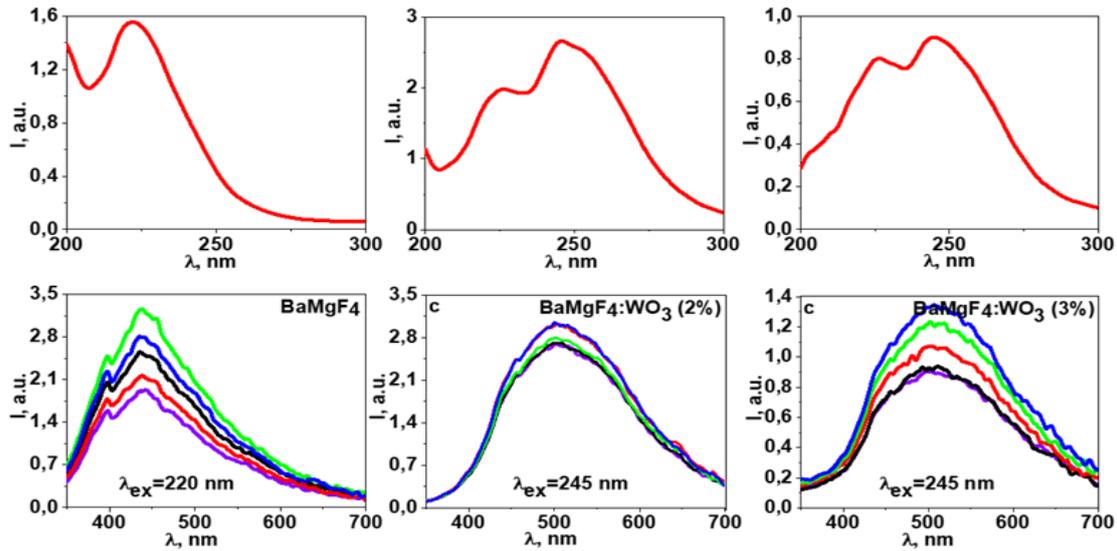


Figure 4. PL spectra of  $\text{BaMgF}_4$  ceramic samples doped with tungsten trioxide. Insert: excitation spectra of the PL emission

Figure 5 shows the results of measuring the excitation and luminescence spectra of  $\text{Ba}_{0.5}\text{Mg}_{1.5}\text{F}_4$  ceramic samples with different tungsten contents. The solid solution of such ceramics is obviously characterized by a nonstoichiometric composition. In the  $\text{BaMgF}_4$  system of stoichiometric composition, a crystal lattice is formed with Ba and Mg ions alternating at cationic sites. In the  $\text{Ba}_{0.5}\text{Mg}_{1.5}\text{F}_4$  system, the lattice consists predominantly of alternating regions with  $\text{BaF}_2$  and  $\text{MgF}_2$  lattices. In such a system, the entry of tungsten ions will be preferable in one of the lattices. The coincidence of the positions of the maxima at 450 nm indicates that W is incorporated into the  $\text{MgF}_2$  lattice, since the  $\text{MgF}_2$  lattice dominates in the system. The broadening of the band indicates that W enters well into the  $\text{BaF}_2$  lattice, although there is a factor of 4 less such phase in the system. Therefore, the inclusion of tungsten substitution of the cation is better implemented in  $\text{BaF}_2$ .

Basically, the trends in the change in the excitation and luminescence spectra are similar to those measured for the  $\text{BaF}_2$ ,  $\text{MgF}_2$ , and  $\text{BaMgF}_4$  systems. There is an expansion to the long-wavelength region of the excitation spectrum upon the introduction of tungsten. The luminescence spectrum shows a complex band with a maximum at about 450 nm, which can be obtained by superimposing the 450 nm band characteristic of the activated  $\text{MgF}_2:\text{W}$  sample and the 500 nm band due to  $\text{BaF}_2:\text{W}$ .

In PL spectra of non-doped samples of  $\text{BaMgF}_4$  ceramics, as well as of doped  $\text{MgF}_2$  ceramics samples the maximum of the broad dominating band with

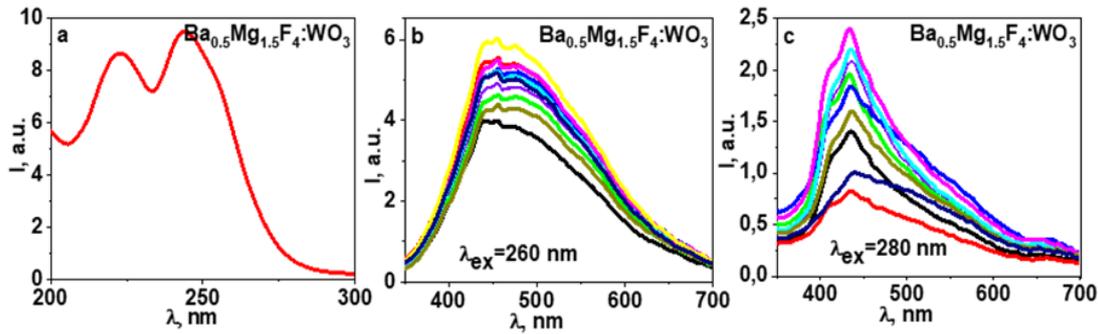


Figure 5. PL spectra of  $\text{Ba}_{0.5}\text{Mg}_{1.5}\text{F}_4$  ceramic samples doped with tungsten trioxide. Insert: excitation spectra of the PL emission

FWHM 0.85 eV occurs at 440 nm. Another common property for these materials is the predominance of the band at 220 nm in the PL excitation spectra.

In the presence of the dopant, band at 250 nm becomes predominant in PL excitation spectra of  $\text{BaF}_2$  and  $\text{BaMgF}_4$  ceramic samples, which seems to be the reason of the appearance of a broad band at 500 nm in the PL spectra of these materials.

## Results and discussion

Thus, the luminescent properties of all ceramic samples obtained from  $\text{BaF}_2$ ,  $\text{MgF}_2$  monopowders or their mix, after adding 2–3%  $\text{WO}_3$  powder to the charge, acquire properties that differ from those in non-doped ceramic samples in terms of the bands ratio in the PL excitation spectra, the position of dominant band maximum in PL spectra, the efficiency of PL excitation.

The presence of tungsten trioxide in the samples leads to the appearance in PL spectra a band in the region of 500 nm in  $\text{BaF}_2$  and  $\text{BaMgF}_4$  ceramic samples. The intensity of the band depends on the level of doping and the wavelength of PL excitation. It was figured out that the 500 nm band intensity depends on the concentration of defects responsible for the band at 250 nm in the excitation spectra of PL.

PL spectra of  $\text{MgF}_2$  ceramic samples are nonuniform broadened in the long-wavelength region  $> 500$  nm and differ from those in other materials under research. Previously [10] it was proved that in the process of synthesis under impact of high-power electron fluxes creation of  $\text{F}_2$  color centers different types occurs in synthesized samples. The band at 590 nm with FWHM of 0.3 eV is one of the bands belonging to these centers. A similar band is observed not only in the  $\text{MgF}_2$  ceramic samples but also in the X-ray luminescence spectrum of the  $\text{MgF}_2$  crystals according to [11].

Based on the results of the conducted research, the following conclusion can be drawn. The impact of high-power electron fluxes with an energy of 1.4 MeV and a power density of  $18 \text{ kW/cm}^2$  on the monopowders of  $\text{BaF}_2$  or  $\text{MgF}_2$  or a mix of these powders leads, with the adding up to 2–3% tungsten trioxide to the charge, to the formation of  $\text{BaF}_2$ ,  $\text{MgF}_2$ , or  $\text{BaMgF}_4$  tungsten-doped ceramics. Ceramics is formed only due to the energy of the radiation flux for a time less

than 1 s, without the adding of any substances facilitating the incorporation of impurities into the matrix. Due to the high rate of synthesis, tungsten ions remain in the composition of the forming ceramic and do not leave the matrix in the form of volatile compounds of tungsten fluoride.

## Acknowledgments

This research has been funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP14871114).

This research was supported by TPU development program.

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