

3-22-2023

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Recommended Citation

Koketai, T.A.; Strelkova, A.V.; Zhunusbekov, A.M.; Karipbayev, Zh.T.; Lisitsyna, L.A.; and Chakin, A.M. (2023) "Luminescent properties of $BaxMg(2-x)F4:W$ ceramics," *Eurasian Journal of Physics and Functional Materials*: Vol. 7: No. 1, Article 2.

DOI: <https://doi.org/10.32523/ejpfm.2023070103>

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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 LiF , MgF_2 , 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/cm³ 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 cm³ was poured into the cavity of 0.7 cm deep in a massive copper crucible with dimensions of 110 × 50 × 40 mm³. 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/cm² from the ELV-6 accelerator. An electron beam having Gaussian space distribution and a cross section of 0.5 cm² 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 MgF_2 , BaMgF_4 ceramics samples, they had irregular oval shapes from 35 to 5 mm² in size. Thickness of the samples reached 5 mm.

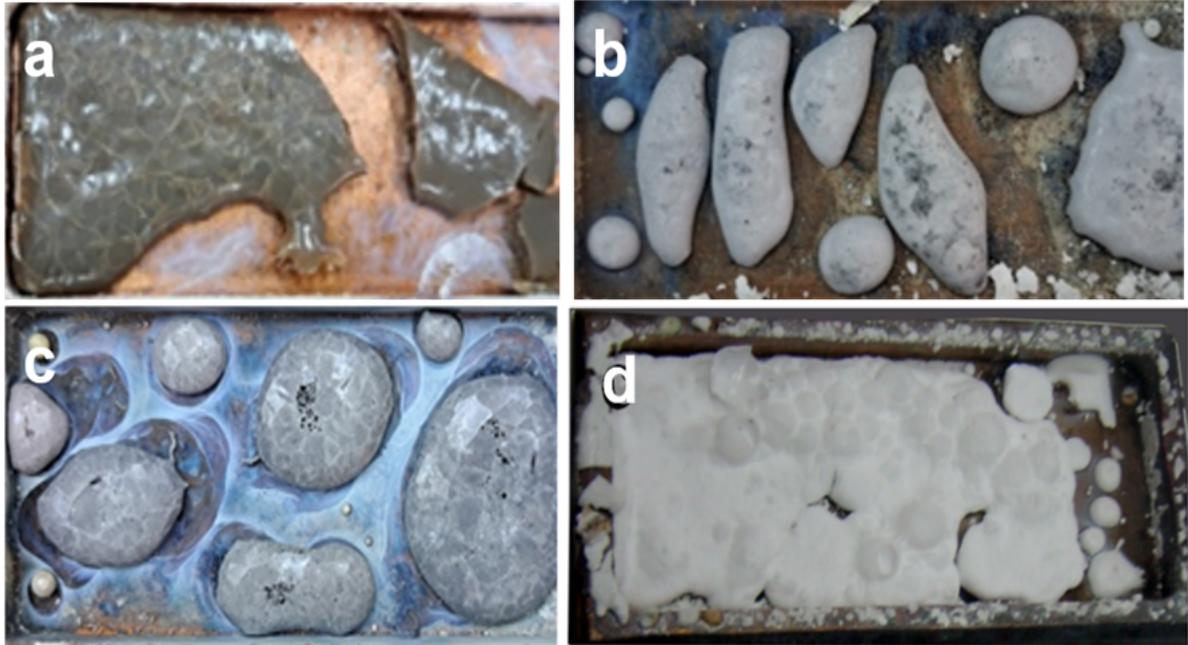


Figure 1. View of as-synthesized samples in crucibles: BaF_2 (a), MgF_2 (b) and $\text{BaMgF}_4:\text{W}$ (c), $\text{Ba}_{0.5}\text{Mg}_{1.5}\text{F}_4$ (d)

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 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 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.

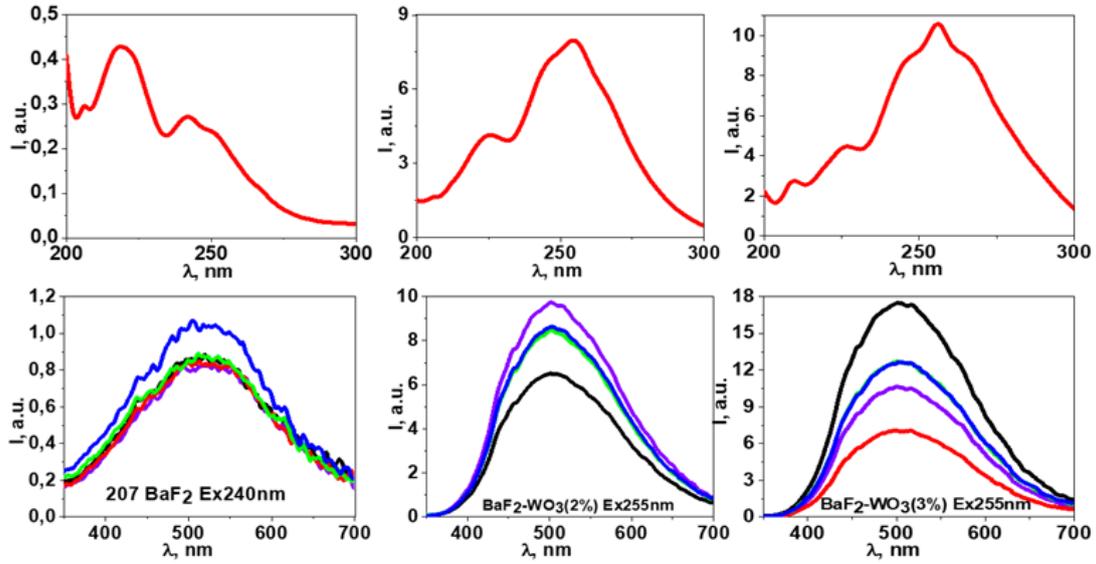


Figure 2. PL spectra of BaF_2 ceramic samples doped with tungsten trioxide. Inserts: excitation spectra of the PL emission

The results of studying the PL of MgF_2 and BaMgF_4 ceramic samples are presented in the Figure 3 and Figure 4.

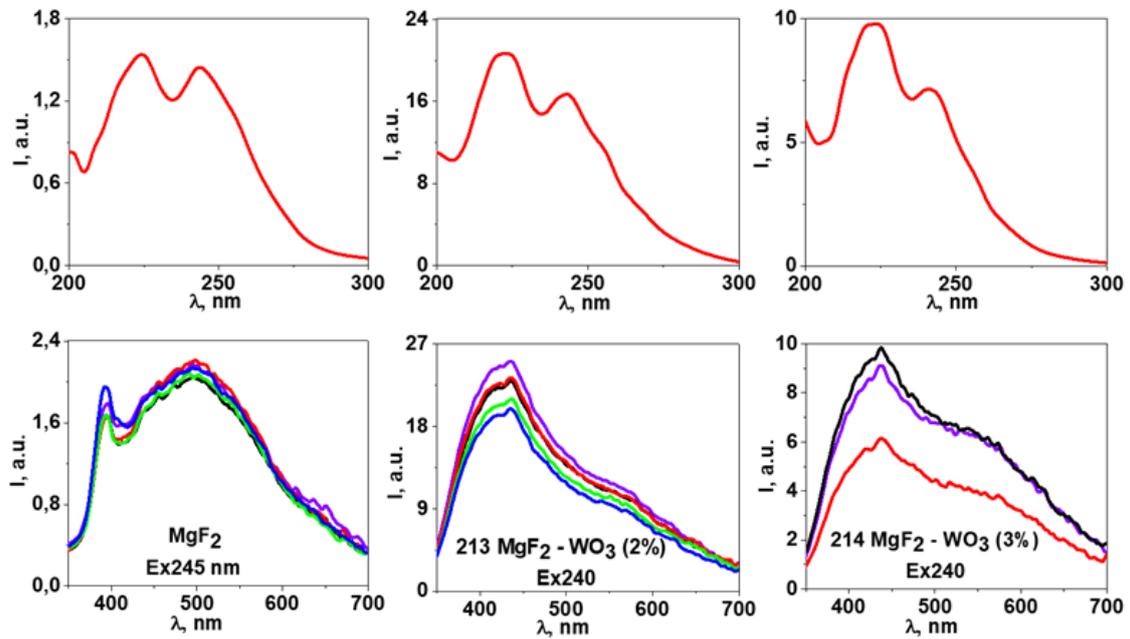


Figure 3. PL spectra of MgF_2 ceramic samples doped with tungsten trioxide. Inserts: excitation spectra of the PL emission

The PL spectra of MgF_2 ceramic samples differ from those measured in BaF_2 . The PL spectra in 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 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 BaF_2 and in MgF_2 ceramic samples are similar and consist of two bands at 220 and 250 nm. In contrast to ceramics based on

BaF_2 , the band at 220 nm in excitation spectra of 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 BaMgF_4 samples doped with WO_3 shown in Figure 4, similar to the PL spectra in doped BaF_2 samples ceramics and consist of an emission band with a maximum in the region of 500 nm.

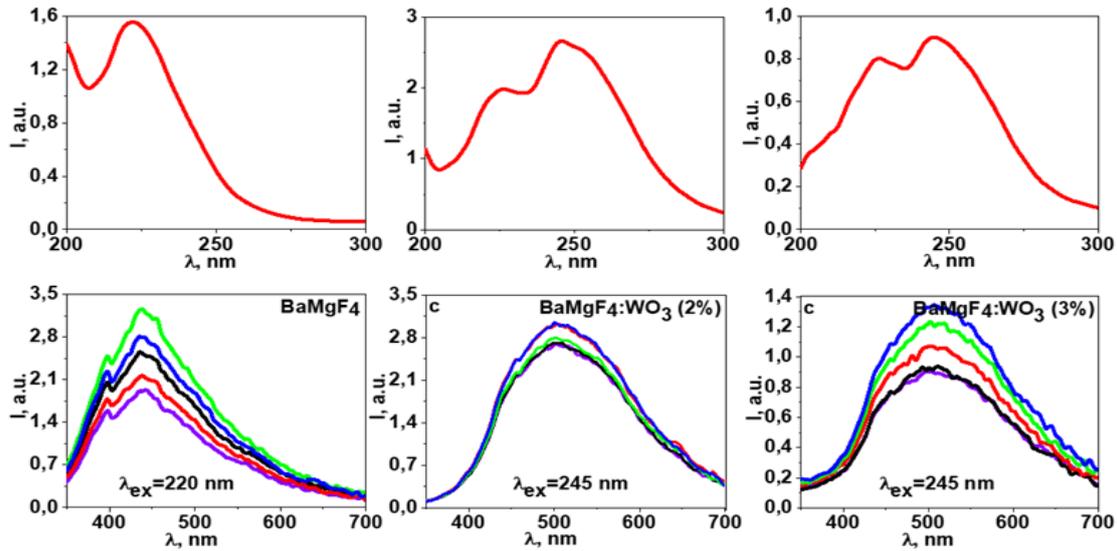


Figure 4. PL spectra of BaMgF_4 ceramic samples doped with tungsten trioxide. Insert: excitation spectra of the PL emission

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 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 BaF_2 and 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 MgF_2 lattice, since the MgF_2 lattice dominates in the system. The broadening of the band indicates that W enters well into the 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 BaF_2 .

Basically, the trends in the change in the excitation and luminescence spectra are similar to those measured for the BaF_2 , MgF_2 , and 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 BaMgF_4 ceramics, as well as of doped MgF_2 ceramics samples the maximum of the broad dominating band with

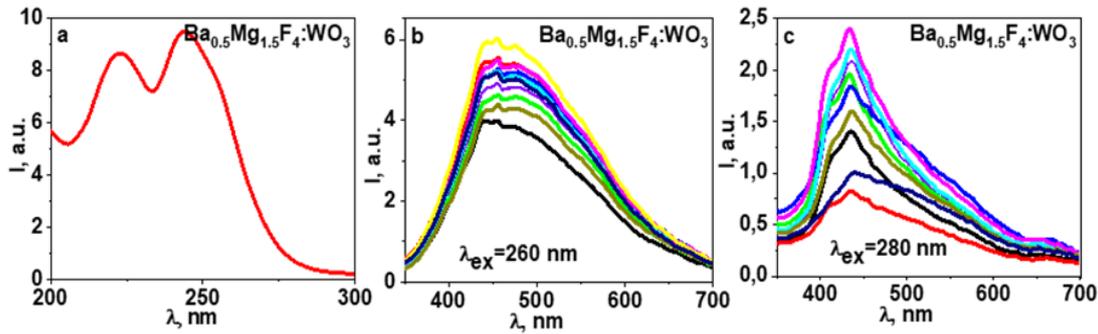


Figure 5. PL spectra of $\text{Ba}_{0.5}\text{Mg}_{1.5}\text{F}_4$ ceramic samples doped with tungsten trioxide. Insert: excitation spectra of the PL emission

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 BaF_2 and 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 BaF_2 , MgF_2 monopowders or their mix, after adding 2–3% 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 BaF_2 and 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 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 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 MgF_2 ceramic samples but also in the X-ray luminescence spectrum of the 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 kW/cm^2 on the monopowders of BaF_2 or 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 BaF_2 , MgF_2 , or 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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