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Dependence of the Radiation Synthesis Efficiency of Ceramics Based on Tungstates on the Flow Power

Ceramic samples of monocomponent (CaO, MgO, ZnO and WO_3) and two-component ($ZnWO_4$, $MgWO_4$, $CaWO_4$) compositions were synthesized by direct impact of high-energy electron flow on the charge of stoichiometric composition. Radiation synthesis of samples weighing about 50 g is realized in time of 10s without the use of any additional substances to stimulate the process. Systematic studies of the dependence of radiation synthesis of tungstate ceramics on the flux power density have been performed for the first time. It was found that the dependences of synthesis efficiency on the flux power density of monocomponent (CaO, MgO, ZnO and WO_3) and two-component ($ZnWO_4$, $MgWO_4$, $CaWO_4$) ceramic samples have the form of constantly increasing curves. There is a threshold above which the synthesis is realized for all synthesized samples. The effect of mutual influence of charge components on the efficiency of synthesis of two-component systems was found. Synthesis of $ZnWO_4$, $MgWO_4$, $CaWO_4$ ceramics is realized under the same conditions of radiation treatment, while the thresholds of synthesis realization of one-component samples of CaO, MgO and ZnO and WO_3 ceramics differ significantly. It is shown that at all used modes of radiation treatment the formation of ceramics with the same properties are realized. This effect is due to the inhomogeneous distribution of electron flux energy losses in the substance. Synthesis of two-component ($ZnWO_4$, $MgWO_4$, $CaWO_4$) ceramic samples is realized at the same power density above 1,0 kW/cm^2. The radiation synthesis of the $ZnWO_4$, $MgWO_4$, $CaWO_4$ ceramics is mainly determined by tungsten oxide.

Keywords: ceramics; metal tungstate, luminescence; radiation synthesis, X-ray diffraction spectra, EDX analysis, power density, optical properties of ceramics

Introduction

Crystals and ceramics based on tungstate of alkaline-earth and rare-earth metals have found wide application as scintillation materials [1–3]. These materials have high absorption capacity of radiation, are resistant to external factors: temperature, aggressive media. They can be used both for registration of heavy particles, electrons and X-ray radiation [4–7].

Synthesis of these materials from metal oxides with high melting point is difficult. Moreover, the melting point of the main initial component, WO_3 (1473 °C), differs significantly from the melting points of other components, such as MgO (2825 °C), ZnO (1975 °C), CaO (2572 °C). Therefore, the synthesis methods used, most often Czochralski and Bridgman [8–11], are labor-intensive, time-consuming, and require the use of other substances to stimulate synthesis.

Radiation method is promising for the synthesis of ceramics based on metal oxides, fluorides. It realized and described first time in [12–14]. The radiation method showed that the impact of a powerful flow of electrons with an energy of 1.4, 2.5 MeV t power density up to 30 kW/cm^2 on the charge stoichiometric

composition is possible to form ceramics based on metal oxides, including tungstate. It is established that the synthesis is realized by direct impact of the electron flux on the charge in the crucible for a time less than 1 s, with high efficiency, without the use of any additional substances that contribute to the process.

The present work is aimed at studying the dependence of the synthesis efficiency on the radiation ion treatment modes, in particular, on the power density of the electron flux falling on the charge.

Experimental

Radiation synthesis of ceramics was realized by direct impact of a powerful flow of high-energy electrons on the charge. The synthesis of materials was carried out by direct electron beam irradiation using the ELV6 electron accelerator at the facility UNU Stand ELV-6 of Budker Institute of Nuclear Physics, of the Siberian Branch of the Russian Academy of Sciences Novosibirsk, Russian Federation. The ELV-6 electron accelerator provides generation of electron flux with energies in the range from 1.4 to 2.5 MeV and power up to 100 kW. The electron beam output through the differential pumping system has a Gaussian distribution in cross-section. In our experiments, the beam area on the charge surface in the crucible was 1 cm^2. A scanning system was used for obtaining large area samples. The beam was scanned at a frequency of 50 Hz across the mixture surface in the transverse direction of a crucible with a width of 5 cm and a length of 10 cm. The crucible was displaced relative to the scanning beam at a speed of 1 cm/s for the entire length of the crucible. Each elementary section of the charge in the crucible was exposed to the radiation flux for 1 s. The total time of exposure of the electron flux to the treated surface of the charge in the crucible was always 10 s. The synthesis of ceramics was realized only due to the energy of the radiation flux, only from the charge materials, without additives of other materials facilitating the process.

Measurements of dispersity of initial powders used for synthesis of initial powders for obtaining ceramic samples were carried out by laser diffraction method using a laser particle size analyzer Shimadzu SALD-7101.

The X-ray diffraction patterns were obtained using a Bruker D8 ADVANCE (AXS, Berlin, Germany) diffractometer equipped with a scintillation detector.

The luminescence of the synthesized samples (luminescence excitation spectra and luminescence spectra) were measured using a Cary 5000 UV-Vis-NIR spectrophotometer.

Results and Discussion

Mixtures of WO_3, MgO, ZnO, CaO starting powders in stoichiometric ratio were prepared for synthesis. All the starting powders were obtained from Hebei Suoyi New Material Technology Co., Ltd, had a purity degree of at least 99,95 %.

It was shown in [15] that the results of radiation synthesis are largely determined by the prehistory of the starting materials, not only their purity but also their particle size distribution. All starting materials have significantly different melting temperatures [16]. In this connection, we investigated the particle size distribution and performed radiation synthesis of each of the starting materials prior to the synthesis of multicomponent ceramics.

The results of the particle size distribution study are shown in Figure 1. The figures show the distribution of particles in the used powders in the form of dependence of the number of particles on their size and dependence of the volume of the particles.

There are two groups of particles with sizes from 0,01 to 1 μm and from 1 μm to 50 μm for all powders. The number of small particles is dominant, but in the total volume of powders their volume is much smaller. Therefore, the synthesis result should be determined mainly by the number of the large particles. The ratio between the number of small and large particles in powders of different composition differs. As follows from the presented results, the distributions of large particles of ZnO and MgO overlap with the distribution of WO_3 particles. The size distribution range of large CaO particles is much wider than that of WO_3. We can expect a difference in the efficiency of synthesis of ceramics of tungstates of these two groups: a large difference in the size of the initial particles may appear in the express synthesis due to the existence of local non-stoichiometry [14].

The starting materials for the synthesis of two-component metal tungstate ceramics have significantly different melting points: WO_3 (1473 °C), MgO (2825 °C), ZnO (1975 °C), CaO (2572 °C), which can affect the efficiency of their synthesis [17]. However, for radiation synthesis, ionization processes play a dominant role in the formation of a new structure from the initial ones, while thermal processes contribute to their efficiency. It seems necessary to study the efficiency of radiation synthesis of ceramics of starting materials. We

have carried out a series of studies of the dependence of the synthesis of ceramics from starting materials on the power density of the radiation flux. The charge for synthesis was simply initial powders of WO_3, ZnO, MgO, CaO. Radiation treatment of the charge was carried out under the conditions mentioned above in the "without scanning" mode. The dependence of the morphology of synthesized samples on the modes of radiation exposure and electron flux power density is shown in Figure 2.

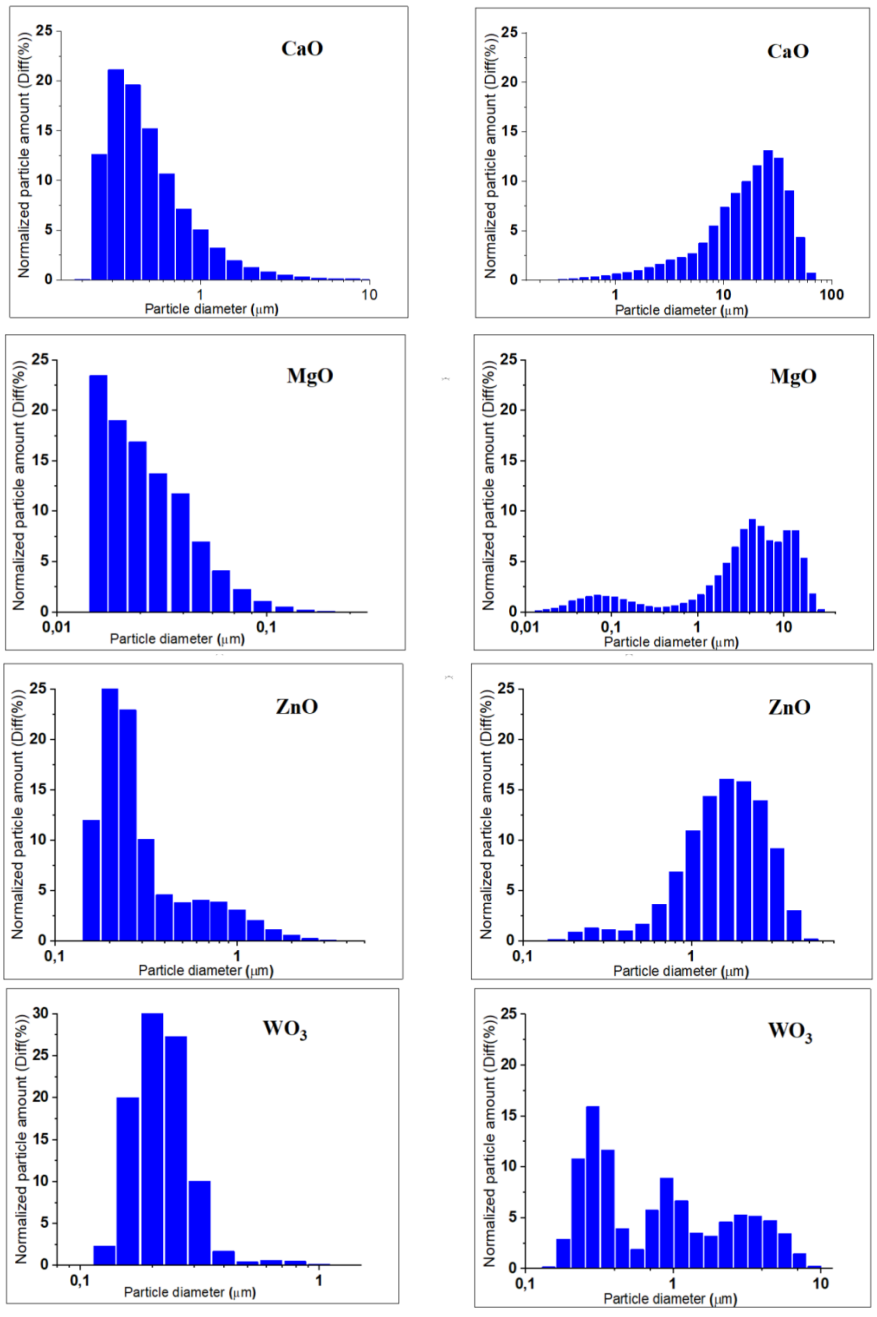

Figure 1. Particle number and volume distribution of the used powders

Figure 2 shows photos of ceramic samples from the initial materials. The value of power density is indicated in the figures. As follows from the presented photos for monocomponent ceramic samples, the dependence of the synthesis result on the electron flux power density is clearly visible. Especially clearly this dependence is seen on the example of WO_3 and ZnO. This dependence is less pronounced in the synthesis of CaO ceramics. Synthesized MgO ceramics has high power densities, but the ceramic samples are formed under the surface of the charge, because the bulk density of the MgO charge (ρ=0.5 g/cm^3) is much less than WO_3 (ρ=2.6 g/cm^3) and ZnO (ρ=1.1 g/cm^3). WO_3 and ZnO differ significantly from MgO and CaO in melt-

ing temperatures. For CaO, a picture of a sample obtained using the “with scanning” mode is given as an example. The synthesis of ceramics from the whole charge in the crucible is realized in this mode. Accordingly, in order to fulfill the equality of absorbed energy in both modes, the power density in the “with scanning” mode is increased by a factor of 5.

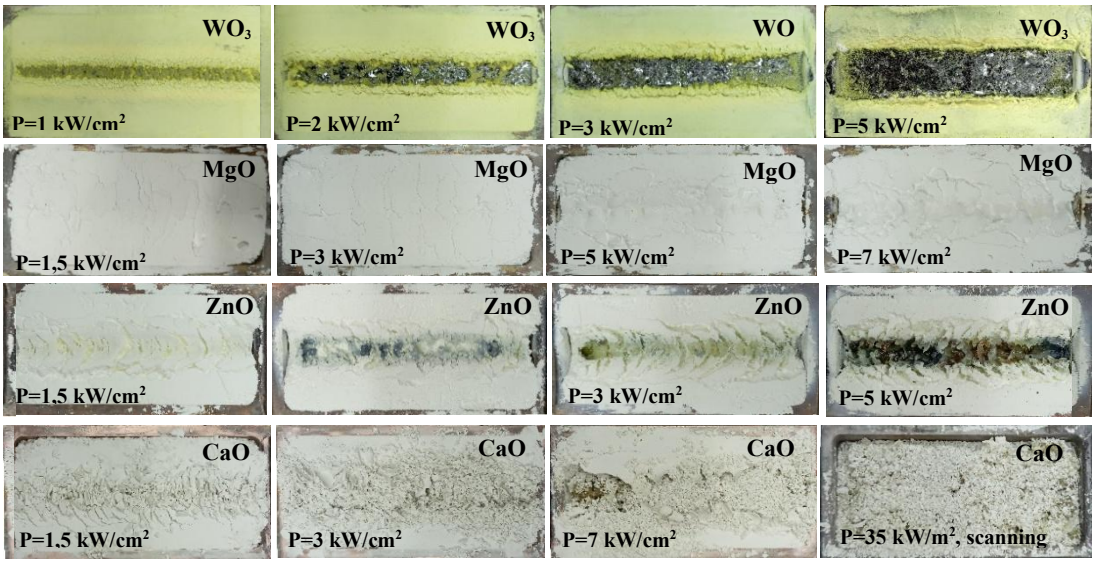

Figure 2. Dependence of morphology of synthesized samples on radiation exposure modes-electron flux power density

Quantitative dependences of synthesis efficiency on power density in the studied monocomponent compositions are shown in Figure 3. Synthesis efficiency in this work is understood as the weight of the synthesized sample. Such characterization of the process seems to be quite justified: the charge volume in our work is always the same using the same crucibles.

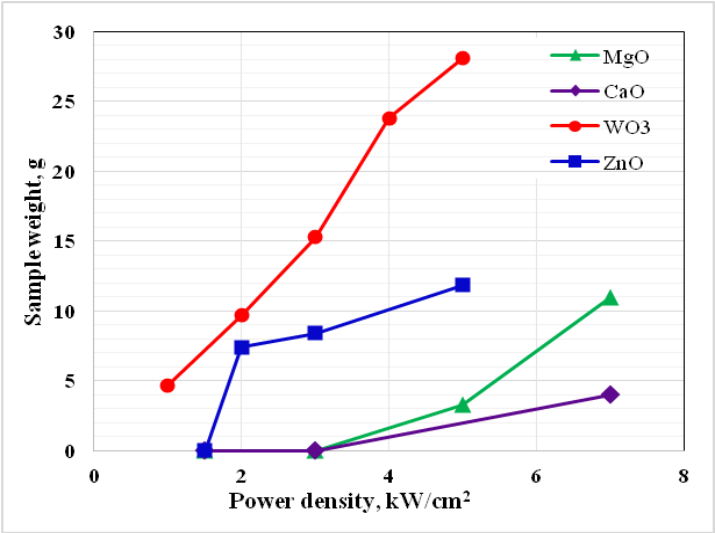

Figure 3.Dependence of ceramic synthesis efficiency from used initial monocomponent compositions on power density

The synthesis of WO_3 and ZnO ceramics is realized when the power density exceeds 1–1.5 kW/cm^2, whereas for the synthesis of MgO and CaO ceramics, power densities above 2.5 kW/cm^2 are required.

We consider that it is necessary to emphasize the following. To determine the weight of the synthesized sample using the “without scanning” mode, the sample is removed from the crucible and cleaned from the charge adhering to it. This procedure is easily realized when the charge is treated with high power radiation

fluxes. It is impossible to clean the completely porous sample from the charge at low power densities. Therefore, the initial points on the dependences are determined with some error. Nevertheless, the full dependence quite unambiguously indicates that the threshold for the realization of the synthesis of WO_3 and ZnO ceramics is lower than that of MgO and CaO. It is necessary to pay attention to the existence of a constant growth of the sample weight at high power density. The growth of the sample weight is due to the increase of the sample area, as it is clearly seen for WO_3 and ZnO. The growth of the bandwidth of the formed ceramics is due to the fact that the electron beam has a Gaussian distribution. As the integral power of the beam increases, the width of its impact region increases with exceeding the threshold for synthesis, as can be seen from Figure 2.

A charge was prepared from the above described monocomponent metal oxides and radiation synthesis was performed. The charge was prepared from oxide powders in stoichiometric ratio. Table 1 describes the compositions prepared for synthesis, radiation treatment modes used for synthesis, electron flux power density. The sample number means the serial number of the experiment according to the accounting system adopted by the authors. The masses of the charge in the crucible and the yield of the synthesis reaction are also given. Here, the yield of the synthesis reaction is understood as the ratio of the mass of the sample to the mass of the charge used. The synthesis was carried out in the "scanning" mode.

Table 1

Composition of synthesized ceramics when treated with 1.4 MeV electron flow

Sample, №	Sample description	P, kW/cm^2	M_s, g	Output, %
623	$ZnWO_4$ (ZnO 26 %), (WO_3 74 %)	15	64,63	91,29
624	$MgWO_4$ (MgO 14,8 %), (WO_3 85,2 %)	15	47,31	97,17
625	$CaWO_4$ (CaO 19,5 %), (WO_3 (80,5 %)	15	39,46	73,28
627	$ZnWO_4$ (ZnO 26 %), (WO_3 74 %)	15	62,56	93,36
738	$MgWO_4$ (MgO 14,8 %), (WO_3 85,2 %)	18	36,99	98,8
718*	$ZnWO_4$ (ZnO 26 %),(WO_3 74 %)	22	86,62	90,0
**Note* – 718 was obtained at an electron beam energy of 2.5 MeV.				

Figure 4 shows photos of samples of synthesized ceramics in standard crucibles with internal dimensions of 100×50 mm.

Figure 4. Photos of samples of synthesized ceramics with numbers 623, 624, 625, 627, 718, 738 (Table 1)

The samples have the form of plates similar to solidified molten mass, about 5 mm thick, with a porous structure inside. Not the entire volume of the charge is involved in the synthesis of ceramics. They use three types of crucibles differing in depth: 7, 10 and 14 mm. For each experiment, differing in the composition of the synthesized ceramics, its bulk density, and electron energy, the one is chosen at which the electrons of the beam will be completely absorbed by the charge. Otherwise, atoms (ions) from the crucible will be introduced into the formed ceramics. Therefore, there always remains a layer of unused charge under the formed ceramics. Part of the charge may disappear during radiation treatment, atomized due to charging of particles by the electron beam. This process can be significant at low mass of dielectric particles of initial substances. We take into account in determining the yield of the synthesis reaction the existence of residues of the charge in the crucible and atomization during radiation treatment.

As can be seen in Table 1, the yield of the synthesis reaction in all samples synthesized in the "with scanning" mode has a value ranging from 73 % to 98 %. Two reasons for this difference are possible. CaO (2572 °C) has a melting point higher than ZnO (1975 °C) and WO_3 (1473 °C). But MgO (2825 °C) also has a melting point higher than ZnO and WO_3. Another factor that differentiates the starting materials is the difference in particle size distribution. In the dispersion spectra (Fig. 1), the number and volume of particles with sizes above 10 μmare are much larger in CaO than in WO_3, MgO and ZnO. It seems to us that this characteristic can determines the difference in the yields of the material synthesis reaction. Nevertheless, we do not deny the influence of the difference in melting temperatures on the synthesis process.

Studies of the dependence of the synthesis efficiency of $ZnWO_4$, $MgWO_4$, $CaWO_4$ ceramics in the "without scanning" mode were performed, as well as for monocomponent compositions shown in Figure 3. The results of the studies are presented in Table 2 and Figure 5. The weight of $CaWO_4$, $MgWO_4$, $ZnWO_4$ tungstate ceramics samples was measured during synthesis without scanning at different electron beam power densities with E=1.4 MeV.

Table 2

Efficiency of synthesis of tungstate ceramics

Power P, kW	Weight of $CaWO_4$, g	Weight of $MgWO_4$, g	Weight of $ZnWO_4$, g
1,5	8,74	11,07	9,57
2	12,97	14,55	13,47
3	16,88	18,26	20,14

Weight dependence of $CaWO_4$, $MgWO_4$ and $ZnWO_4$ tungstate ceramics during synthesis without scanning at different electron beam power densities with E=1.4 MeV.

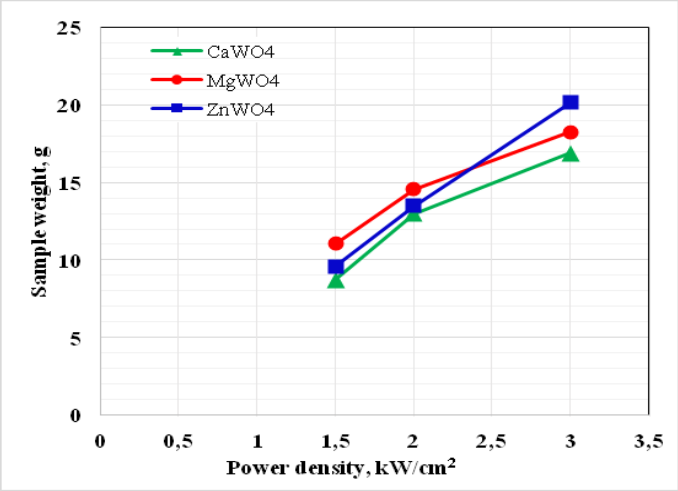

Figure 5. Weight dependence of $CaWO_4$, $MgWO_4$, $ZnWO_4$ tungsten ceramics on electron flux power density

As follows from the presented results, synthesis in all investigated samples of multicomponent ceramics is realized at the same regimes of radiation treatment. We emphasize that ceramics of monocomponent samples is realized at different regimes for CaO, MgO, WO_3 and ZnO. Note that equal conditions of electron beam energy losses during radiation treatment in the "without scanning" mode, for example 1.5 kW/cm^2, corresponds to 7–85 kW/cm^2 in the "with scanning" mode.

The structure of synthesized samples of $ZnWO_4$, $CaWO_4$ ceramics was studied by X-ray diffraction using a Bruker D8 ADVANCE diffractometer (AXS, Berlin, Germany) equipped with a scintillation detector in step-scan mode over a diffraction angle range of 10 to 90° 2θ and CuKα radiation as the source. Details of the research methodology and analysis are described in [15].

The results of the X-ray powder diffraction investigation are presented in Table 3. The qualitative phase analysis and indexing of the diffraction patterns utilized the data from the PDF-2 database (ICDD, 2007) as follows:

- PDF 01-088-0251 "Zinc tungsten oxide ($ZnWO_4$)", symmetry — monoclinic lattice, space group — *P2/c* (#13), a = 4.6926 Å, b = 5.7213 Å, c = 4.9281 Å, β = 90.632 °.

- PDF 01-072-0257 “Calcium tungsten oxide ($CaWO_4$)”, symmetry — body-centered tetragonal lattice, space group — $I41/a$ (#88), a = 5.243 Å, c = 11.376 Å.

- PDF 01-072-0677 “Tungsten oxide (WO_3)”, symmetry — monoclinic lattice, space group — $P21/n$ (#14), a = 7.306 Å, b = 7.54 Å, c = 7.692 Å, β = 90.881 °.

Table 3

The results of the phase composition investigation

Sample	Phase	Degree of crystallinity	Crystallite size	Refined unit cell parameters
$ZnWO_4$	$ZnWO_4$	99.9 (±5) %	131 (±15) nm	$P2/c$, a = 4.689(4) Å, b = 5.716(7) Å, c = 4.925(3) Å, β = 90.6(1) °, V = 132.0(1) Å^3
$CaWO_4$	$CaWO_4$ (~86 %)	99.9 (±5) %	167 (±35) nm	$I41/a$, a = 5.243(2) Å, c = 11.371(4) Å, V = 312.5(2) Å^3
	WO_3 (~14 %)		114 (±28) nm	$P21/n$, a = 7.311(2) Å, b = 7.532(2) Å, c = 7.694(2) Å, β = 90.8(1) °, V = 423.6(1) Å^3

The results of the study of $MgWO_4$ ceramics are not presented due to the absence of complete data on this material in our database [18]. As can be seen from the results presented in the table, during radiation synthesis in the samples ceramics formed crystalline phase in the form of crystallites with sizes of 100–170 nm. The dominant phase is $ZnWO_4$, $CaWO_4$ ceramics, with WO_3 as the accompanying phase [19].

The main functional characteristic of metal tungstates is luminescence and its properties [20]. Excitation and luminescence spectra were measured for $ZnWO_4$, $MgWO_4$, $CaWO_4$ ceramics samples [21]. The excitation and photoluminescence spectra were measured on a SM-2203 Solar spectrofluorimeter. Figure 6 shows the excitation and luminescence spectra of $ZnWO_4$, $MgWO_4$, $CaWO_4$.

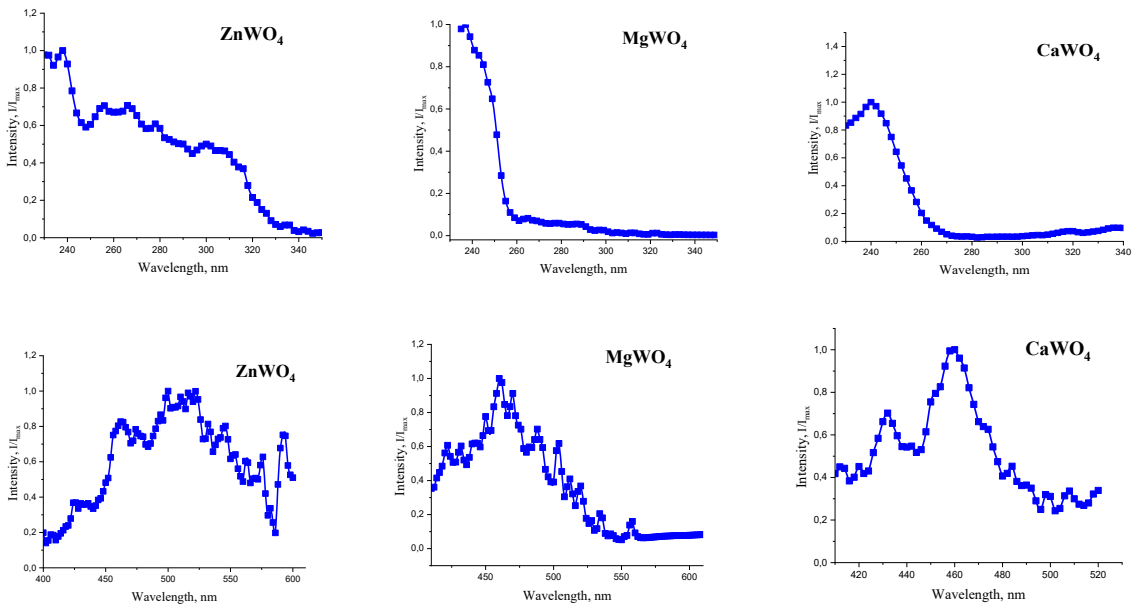

Figure 5. Excitation (top) and luminescence (bottom) spectra of $ZnWO_4$, $MgWO_4$, $CaWO_4$, respectively

In $ZnWO_4$ ceramics luminescence is excited by UV radiation from 230 to 320 nm, in $MgWO_4$230–250 nm, in $CaWO_4$ 230–260 nm [22]. The luminescence maxima occur in $ZnWO_4$ at 500 nm, in $MgWO_4$, at 460 nm, in $CaWO_4$ at 460 nm. In general, the spectral characteristics of photoluminescence correspond to those known for crystalline materials [23].

Conclusion

For the first time, systematic studies of the dependence of radiation synthesis of tungstate ceramics on the conditions of radiation treatment have been performed. The dependence of synthesis efficiency on the power density of high-energy electron flux of monocomponent (CaO, MgO, ZnO and WO_3) and two-component ($ZnWO_4$, $MgWO_4$, $CaWO_4$) ceramic samples has been established. It is shown that these dependences have the form of continuously increasing curves. Nevertheless, for all synthesized samples there is a threshold above which the synthesis is realized. The knowledge of thresholds and dependence on the electron flux power density allows us to choose the optimal conditions for the synthesis realization and contributes to the development of ideas about the processes in the charge in the radiation field that ensure the formation of ceramics.

The effect of the mutual influence of charge components on the synthesis efficiency of two-component systems is of interest. Synthesis of $ZnWO_4$, $MgWO_4$, $CaWO_4$ ceramics is realized under the same conditions of radiation treatment, while the thresholds for the synthesis of single-component CaO, MgO, ZnO and WO_3 ceramics samples differ significantly.

It is shown that at all used modes of radiation treatment the formation of ceramics with the same properties are realized. This effect is due to the inhomogeneous distribution of electron flux energy losses in the substance.

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Вольфрамат негізіндегі керамиканың радиациялық синтезінің тиімділігінің ағын қуатына тәуелділігі

Монокомпонентті (CaO, MgO, ZnOжәнеWO3) және екікомпонентті ($ZnWO_4$, $MgWO_4$, $CaWO_4$) композициялардың керамикалық үлгілері стехиометриялық құрамның шихтасына жоғары энергиялы электрон дарағының тікелей әсері арқылы синтезделді. Салмағы шамамен 50 г болатын үлгілердің радиациялық синтезі процесті ынталандыру үшін кез келген қосымша заттарды қолданбай 10 с уақыт ішінде жүзеге асырылады. Алғаш рет вольфрамат керамикасының радиациялық синтезінің ағын қуатының тығыздығына тәуелділігі туралы жүйелі зерттеулер жүргізілді. Синтез тиімділігінің біркомпонентті (CaO, MgO, ZnO және WO_3) және екікомпонентті ($ZnWO_4$, $MgWO_4$, $CaWO_4$) керамика үлгілерінің ағынының тығыздығына тәуелділігі үнемі өсіп келе жатқан қисықтар түрінде болатындығы анықталды. Барлық синтезделген үлгілер үшін шекті мән бар, оның үстінде синтез жүзеге асырылады. Екікомпонентті жүйелердің синтезінің тиімділігіне шихта компоненттерінің өзара әсерінің әсері анықталды. $ZnWO_4$, $MgWO_4$, $CaWO_4$ керамикасының синтезі бірдей жағдайларда, радиациялық өңдеуде жүзеге асырылады, ал CaO, MgO және ZnO және WO_3 керамикасының

біркомпонентті үлгілерін синтездеу шектері айтарлықтай ерекшеленеді. Радиациялық өңдеудің барлық қолданылған режимдерінде бірдей қасиеттері бар керамиканың қалыптасуы жүзеге асырылатындығы көрсетілген. Бұл әсер заттағы электрондар ағынының энергия шығынының гетерогенді таралуына байланысты.

Кілт сөздер: керамика, металл вольфраматы, люминесценция, радиациялық синтез, рентген дифракциясының спектрлері, EDX-талдау, қуат тығыздығы, керамиканың оптикалық қасиеттері.

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Зависимость эффективности радиационного синтеза керамики на основе вольфраматов от мощности потока

Синтезированы образцы керамики монокомпонентных (CaO, MgO, ZnO и WO_3) и двухкомпонентных ($ZnWO_4$, $MgWO_4$, $CaWO_4$) составов посредством прямого воздействия потока высокоэнергетических электронов на шихту стехиометрического состава. Радиационный синтез образцов весом около 50 г реализуется за время 10 с без использования любых дополнительных веществ для стимуляции процесса. Впервые выполнены систематические исследования зависимости радиационного синтеза керамики вольфраматов от плотности мощности потока. Установлено, что зависимости эффективности синтеза от плотности мощности потока монокомпонентных (CaO, MgO, ZnO и WO_3) и двухкомпонентных ($ZnWO_4$, $MgWO_4$, $CaWO_4$) образцов керамики имеют вид постоянно нарастающих кривых. Для всех синтезированных образцов имеет место наличие порога, выше которого синтез реализуется. Обнаружен эффект взаимного влияния компонентов шихты на эффективность синтеза двухкомпонентных систем. Синтез $ZnWO_4$, $MgWO_4$, $CaWO_4$ керамики реализуется при одинаковых условиях, радиационной обработки, тогда как пороги реализации синтеза однокомпонентных образцов керамики CaO, MgO и ZnO и WO_3 существенно различаются. Показано, что при всех использованных режимах радиационной обработки реализуется формирование керамики с одинаковыми свойствами. Обусловлен этот эффект неоднородным распределением потерь энергии потока электронов в веществе.

Ключевые слова: керамика, вольфрамат металла, люминесценция, радиационный синтез, спектры рентгеновской дифракции, EDX-анализ, плотность мощности, оптические свойства керамики

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