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Luminescence of ZrO_2 compacts irradiated with high energy ions [1]

Abstract: phosphors based on zirconium dioxide of various phase composition, widely used in modern technology, should have high stability of characteristics under various radiation effects. This is especially important when used in military and space technology, as well as in the nuclear industry. The determining factor influencing the stability of the luminescence properties of oxide dielectrics under irradiation is the formation of radiation-induced defects. The study of synthesized compacts and ceramics based on ZrO_2 is necessary to predict and improve the radiation resistance. This paper presents the results on the synthesis of zirconium dioxide compacts. The compacts were synthesized by pressing in the form of tablets under pressure in the range of 900-1500 kgf/cm^2. The nanopowder of ZrO_2 consisted of 100% monoclinic phase. The compacts were irradiated with 220 MeV ^{132}Xe and 4.8 MeV ^{14}N ions to fluences (10^{10}-10^{14}) ions/cm^2 at accelerator DC-60 (Nur-Sultan, Kazakhstan). The spectra of photoluminescence (PL), pulsed cathodoluminescence (PCL) and thermoluminescence (TL) were investigated. Degradation of PL and PCL at high fluences is observed. The TL results indicate that ion irradiation leads to a change in the type of trap activation energy dependence on temperature.

Keywords: zirconium dioxide compacts, photoluminescence pulsed cathodoluminescence, thermoluminescence, swift heavy ions.

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Introduction. Zirconium dioxide (ZrO_2) (bandgap E_g = 5.0 - 5.5 eV) is now considered as one of the most important materials used in modern measurement technology, nanoelectronics and photonics [1]. It has a significant luminescence yield, high reflection coefficient, low phonon energy, and high thermal and chemical resistance [2]. ZrO_2-based phosphors are used to manufacture oxygen sensors, biological sensors, laser devices, optoelectronic devices, UV and ionizing radiation dosimeters, scintillators, high-energy radiation imaging devices, etc. [3]. For these applications, an important task is to ensure the stability of the luminescent properties of the material, when exposed to various types of radiation. This problem is especially relevant when using ZrO_2-based devices in military and space technologies, as well as in the nuclear industry.

This paper presents the results on the synthesis of zirconium dioxide compacts and the effect of irradiation with swift heavy ions (SHI) simulating fission fragments on the luminescence properties of the synthesized compacts.

Samples and research methods. To produce nanocompacts, ZrO_2 powders were subjected to cold uniaxial pressing with pressures in the range of 900-1500 kgf/cm^2. The mass of powders of all compacts was 60 mg. The compacts were pressed in the form of a disk with a diameter of 6.1 mm

[1]The work was performed under grant project AP09260057 "Luminescence and radiation resistance of synthesized under different conditions micro - and nanostructured compacts and ceramics based on ZrO_2", MES RK

and height of at least 1 mm. According to the information of the nanopowder manufacturers, ZrO_2 was 100% the monoclinic phase, so the phase composition was not studied by X-ray diffraction in this work.

The samples were irradiated with Xe ions (220 MeV) and N ions (4.8 MeV) at cyclotron DC-60 (INP, Nur-Sultan, Kazakhstan) to fluences (10^{10} - 10^{14}) ions/cm^2 at room temperature.

Excitation and photoluminescence (PL) spectra in this work were measuredby an LS-55 spectrometer at room temperature. The PL was excited by a 150W xenon discharge lamp operating in pulsed mode with a frequency of 50Hz. PL was analysed using a R928 photomultiplier, whose spectral range of sensitivity ranges from 200 to 900 nm with a maximum at 400 nm [4].

Registration of the pulsed cathodoluminescence spectra (PCL) of crystals was performed using a cathodoluminescent pulsed substance analyzer "CLAVI". Luminescence in the samples was excited when compacts were irradiated in air at room temperature with an electron beam of 2 ns duration, with a maximum electron energy of 130 $\pm$ 10 keV and a current density of 60 A/cm^2. The spectral range of registration was from 350 to 750 nm, the spectral resolution was 2 nm.The measurement error of wavelengths at the highest gain position of the electron-optical transducer is $1\lambda = \pm 0.75$ nm [5].

Thermoluminescence (TL) was measured in the linear heating mode at a rate of 2 K/s in the temperature range 60 - 600 $^\circ$C. Photomultiplier -130 (spectral region of sensitivity 200-650 nm with the maximum at 400-420 nm) and Photomultiplier - 142 (spectral region of sensitivity 112-365 nm) were used for registration of TL luminescence. Due to air absorption, the spectral region of sensitivity for the Photomultiplier - 142 is reduced to 200-365 nm.

Results and discussion. The luminescence spectra of the initial and irradiated compacts were measured. It was found that excitation by light with a wavelength of 230 and 280 nm, the PL spectra of the virgin samples show a band with maximum at 480 nm (Figure 1). Irradiation with a beam of ^{14}N ions with a fluence of 10^{14} ions/cm^2 leads to a decrease in the PL 480 nm.

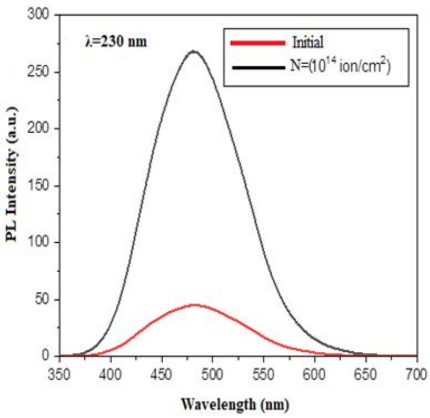

Figure 1 – PL spectra of initial and ^{14}N-irradiated ZrO_2 compacts

The effect of irradiation with 220 MeV ^{132}Xe ions on the luminescence properties of ZrO_2 was also investigated by the PCL method. The pulsed cathodoluminescence spectra of unirradiated compacts were found to contain a luminescence band at 490 nm (Figure 2). Irradiation with a beam of ^{14}N ions with a fluence of 10^{14} ions/cm^2 leads to a decrease in the intensity of luminescence, i.e. to the degradation of luminescent properties of compacts.

It is known that ZrO_2 has a maximum of own luminescence in the wavelength range of 470-490 nm (2.5 - 2.7 eV) [6, 7]. This band is observed in both photoluminescence (PL) and PCL spectra.

Despite the active study of zirconium dioxide luminescence and the large number of publications, there is no consensus in the scientific community about the nature of this luminescence band. There

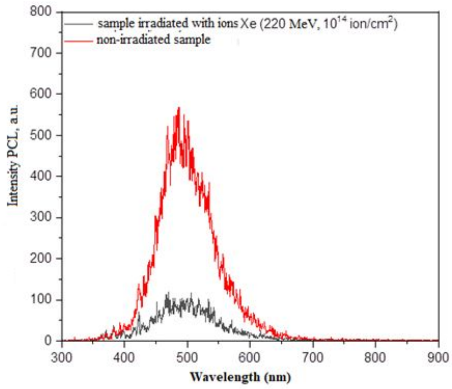

Figure 2 – Pulsed cathodoluminescence spectra of initial and ^{132}Xe-irradiated ZrO_2 compacts

are three main points of view on this issue. The first is that the luminescence band is associated with the presence of Zr^{3+} ions. For example, in [8] the authors suggested that the 480 nm band was associated with the recombination of holes from the valence band with electrons trapped by Zr^{3+} traps, based on the analysis of the optical absorption and EPR spectra of ZrO_2 single crystal irradiated with X-rays to create its own defects.

Another point of view attributes the luminescence of this band to the presence of an uncontrolled Ti^{3+} ion impurity, which is present even in nominally pure ZrO_2 samples [9, 10]. For example, in [11] the authors investigated the effect of Ti and Lu impurities on the luminescent properties of ZrO_2 produced by the sol-gel method and annealed at 1000 $^\circ$C for 5 hours. The alloying of zirconium dioxide samples with Ti (0.5 mole %) leads to a more than 10 - fold increase in the intensity in the luminescence band at 480 nm compared to pure ZrO_2, which confirms the relationship of this band with an admixture of titanium. The authors also performed a comparative analysis of the normalized spectra of pure ZrO_2 and doped samples. This indicates the same nature of the luminescence centers in these samples. A similar increase in the luminescence intensity of the 480 nm ZrO_2 band when doped with Ti was observed in [12]. However, the authors noted that this growth with increasing Ti concentration is not linear. At a concentration of Ti over 0.175%, a sharp decline in band intensity in the excitation and luminescence spectra is observed, indicating an ambiguous influence of the Ti impurity on the luminescence band at 480 nm in ZrO_2. Finally, there is evidence that the 480 nm band in ZrO_2 is associated with the presence of oxygen vacancies in different charge states in the material under study, the so-called F-type centers. It is known that the defects associated with these oxygen vacancies largely determine the optical and luminescent properties of oxides and oxygen-containing compounds [13].

The thermoluminescence (TL) properties of ZrO_2 compacts were investigated to determine the possibility of their use for dosimetry of pulsed electron beams (130 keV, 2 ns). For this purpose, the virgin and irradiated with ion beams (Xe and N) compacts were irradiated with a test dose of 5 kGy from the pulsed electron beam, and then TL measurement was carried out. The TL curves of the virgin and irradiated compacts contained two TL peaks at 330 - 430 K and 430 - 550 K. The peak at 430 - 550 K is the most intense in the original sample. The greatest change in the TL intensity of this peak occurs in the sample irradiated with ^{14}N ions: a 2.3-fold decrease in intensity is observed.

Using the analysis of TL curves recorded during linear heating, the kinetic parameters of the TL peak at 430 - 550 K (kinetic order b, activation energy E and frequency factor S) were determined, the results are shown in Table 1. The order of kinetics was determined through a shape factor (as the ratio of the high-temperature part of the peak width to the full width at half the peak height), the E and S values were calculated by peak shape analysis. It was found that the TL of the virgin and irradiated ^{132}Xe compacts are characterized by close values of the activation energy (1.4-1.5 eV) and the kinetic order (1.6-1.7). The greatest changes in the kinetic parameters compared to the virgin compacts are observed in the samples irradiated with ^{14}N ions. They are characterized by an order of kinetics close to 1 (b = 1.1), indicating that the probability of trap recapture of charge carriers is low.

Table 1 – Kinetic parameters of TL peak at 430 - 550 K

Samples	b	E, eV	S, s^{-1}
Compacts irradiated with ^{132}Xe ions (10^{13} ions/cm^2)	1,7	1,52	9,10·10^{14}
Compacts irradiated with ^{14}N ions (10^{13} ions/cm^2))	1,1	1,28	1,74·10^{12}
Virgin compacts	1,6	1,40	3,07·10^{13}

The trap activation energy responsible for the TL peak at 430 - 550 K was also determined by fractional heating. Figure 3 shows the thermal luminescence curves of the studied samples measured in the fractional heating mode and the change in the activation energy within the specified peak.

The results indicate that ion irradiation leads to a change in the type of trap activation energy dependence on temperature. It was found that in the high-temperature part of the TL peak, the activation energy decreases with increasing temperature, which may indicate the processes of temperature quenching of luminescence.

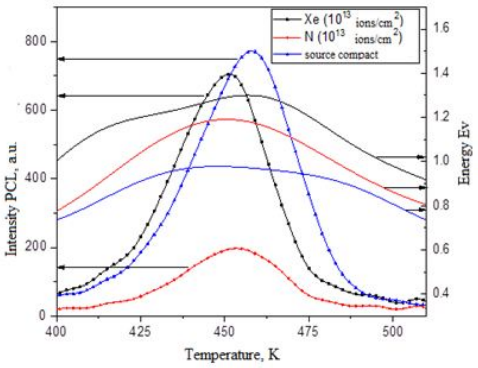

Figure 3 – TL curves of ZrO_2 compacts measured in fractional heating mode and the change in activation energy within the TL peak at 430 – 550 K

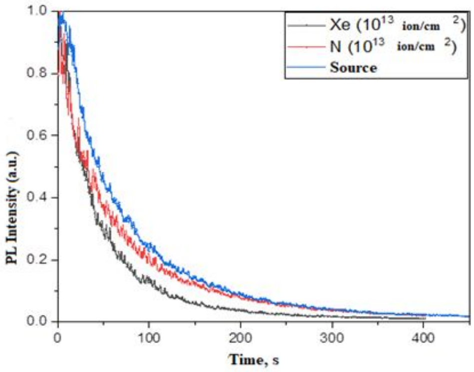

Figure 4 – Isothermal attenuation curves of TL of ZrO_2 compacts measured at 463 K

Isothermal attenuation curves of TL at 463 K were measured for the virgin and irradiated ions (^{132}Xe and ^{14}N, fluence 10^{13} ions/cm^2) compacts (Figure 4). It was found that irradiation with ion beams leads to a decrease in the TL attenuation time; this effect is most noticeable in compacts irradiated with ^{132}Xe ions.

Conclusion. The study of PL and PCL of SHI-irradiated zirconium dioxide compacts shows that at high fluences there is a degradation of luminescent properties of compacts. The TL results indicate that ion irradiation leads to a change in the type of trap activation energy dependence on temperature. It was found that in the high-temperature part of the TL peak, the activation energy decreases with increasing temperature, which may indicate the processes of temperature quenching of luminescence.

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Люминесценция компактов ZrO_2, облученных быстрыми тяжелыми ионами

Аннотация. Люминофоры на основе диоксида циркония различного фазового состава, широко используемые в современной технике, должны обладать высокой стабильностью характеристик, при различных радиационных воздействиях. Это особенно важно при их применении в военной и космической технике, а также в атомной отрасли. Определяющим фактором, влияющим на стабильность люминесцентных свойств оксидных диэлектриков при радиационном воздействии, является образование радиационно-индуцированных дефектов. Исследование синтезированных компактов и керамик на основе ZrO_2 необходимы для прогнозирования и повышения радиационной стойкости ZrO_2. В настоящей работе представлены результаты по синтезу компактов диоксида циркония. Компакты были синтезированы прессованием в форме таблеток под давлением в диапазоне 900–1500 кгс/см^2. Нанопорошок ZrO_2 на 100% состоял из моноклинной фазе. Компакты были облучены ионами 220 МэВ ^{132}Xe и 4.8 МэВ ^{14}N до флюенсов (10^{10} – 10^{14}) ион/см^2 на ускорителе ДЦ-60 (Нур-Султан, Казахстан). Исследованы спектры фотолюминесценции (ФЛ), импульсной катодолюминесценции (ИКЛ) и термолюминесценции (ТЛ). Наблюдается деградация ФЛ и ИКЛ при высоких флюенсах. Результаты ТЛ свидетельствуют о том, что ионное облучение приводит к изменению вида зависимости энергии активации ловушки от температуры.

Ключевые слова: компакт диоксида циркония, фотолюминесценция, импульсная катодолюминесценция, термолюминесценция, быстрые тяжелые ионы.

А. Даулетбекова [1], С. Никифоров [2], С. Звонарев [2], Д. Ананченко [2], Г. Аралбаева [1], Г. Ахметова-Әбдік [1], З. Баймуханов [1], А. Жунусбеков [1]

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Жылдам ауыр иондармен сәулеленген ZrO_2 компакттарының люминесценциясы

Аннотация. Заманауи техникада кеңінен қолданылатын әртүрлі фазалық құрамдағы люминофор негізіндегі цирконий диоксиді әртүрлі радиациялық әсерлер кезінде жоғары тұрақтылық сипаттамаларына ие болуы керек. Бұл көп жағдайда әскери және ғарыштық техникада, сондай-ақ атом өнеркәсібінде қолданылануда аса маңызды. Анықтаушы фактор ретінде радиациялық әсер ету кезінде оксидті диэлектриктердің люминесценттік қасиеттерінің тұрақтылығына әсер ететін радиациядан туындаған ақаулардың пайда болуы болып табылады. Бұл зерттеу ZrO_2 негізінде синтезделген компакттарды және керамикаларды зерттеу ZrO_2 сәулеленуге төзімділігін болжау және жақсарту үшін қажет. Бұл жұмыста цирконий диоксиді компакттарының синтезі бойынша нәтижелер берілген. Компакттер 900-1500 кгс/см^2 диапазонында қысыммен таблеткалар түріндегі сығымдау арқылы синтезделді. ZrO_2 наноұнтағы 100% моноклиникалық фазадан тұрды. Үлгілер ДЦ-60 үдеткішінде (Нұр-Сұлтан, Қазақстан) 220 МэВ ^{132}Xe және 4,8 МэВ ^{14}N иондарымен (10^{10} – 10^{14}) ион/см^2 флюенста сәулелендірілген. Фотолюминесценция (ФЛ), импульстік катодолюминесценция (ПКЛ) және термолюминесценция (ТЛ) спектрлері зерттелді. Жоғары флюенцияларда ФЛ және ПКЛ деградациясы байқалады. ТЛ нәтижелері иондық сәулеленудің температураға тәуелділік қақпаның активтендіру энергиясының түрінің өзгеруіне әкелетінін көрсетеді.

Түйін сөздер: цирконий компакт, фотолюминесценция, импульстік катододолюминесценция, термолюминесценция, жылдам ауыр иондар.

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