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Cathodoluminescence properties of oxide and fluoride ceramics synthesized in the field of high-energy electrons flux

Traditionally, the synthesis of refractory ceramics is a complex and time-consuming process. Some time ago, a new, much faster method was proposed — the method of synthesis of luminescent ceramics in the field of a powerful flux of high-energy electrons. In the synthesis of multicomponent oxide phosphors, it is not an easy task to determine the dependencies of the properties of the resulting material on the composition of the raw mixture and the modes of the synthesis process. In this regard, it seems logical to study the properties of ceramics made by radiation synthesis from simple oxides, which are components of more complex phosphors. An investigation of the spectral and kinetic patterns of cathodoluminescence of ceramic samples of metal oxides (Ga_2O_3, Al_2O_3, Y_2O_3) and fluorides (MgF_2, BaF_2) obtained by radiation synthesis method was carried out. The paper presents an analysis of the cathodoluminescence spectra of the studied samples with the allocation of elementary bands, conclusions about the dynamics of luminescence decay are made. The obtained results are compared with the known data on single crystal samples. It is shown that, unlike oxide ceramics, the spectral characteristics of MgF_2 and BaF_2 ceramic samples show good agreement with the data on single crystals of these compounds.

Keywords: oxide ceramics, fluoride ceramics, cathodoluminescence, radiation synthesis, spectra, time resolution, Ga_2O_3, Al_2O_3, Y_2O_3.

Introduction

YAG ceramics with activators is a promising material, including for use as phosphors for LEDs. The synthesis of refractory ceramics is a complex and time-consuming process. Some time ago, in the works of V.M. Lisitsyn [1, 2], another, much faster method was proposed — the method of synthesis of luminescent ceramics in the field of a powerful high-energy electron flux. The samples for this work were synthesized by direct exposure of the raw materials to an electron beam with an energy of 1.4 MeV and a power density of 20 kW/cm^2, in the mode of scanning electron beam. Each section of the surface of the synthesized substances was exposed to a radiation beam for about 1 s. The total exposure time of the supplied electron beam to the crucible was 10 s. The ELV-6 accelerator at the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences was used for synthesis [1].

The synthesis of oxide ceramics using a fundamentally new technology requires a comprehensive study of the properties of this ceramic. In the synthesis of multicomponent oxide phosphors, it is not an easy task to determine the dependencies of the properties of the resulting material on the composition of the raw mixture and the modes of the synthesis process. In this regard, it seems logical to study the properties of ceramics made by radiation synthesis from simple oxides, which are components of more complex phosphors. The purpose of this work is to study the spectral and kinetic patterns of cathodoluminescence (CL) of ceramic samples of metal oxides and fluorides obtained by radiation synthesis method and compare the results obtained with known data on single crystal samples.

Experimental

Ceramic samples of metal oxides (Ga_2O_3, Al_2O_3, Y_2O_3), including those with an admixture of 0.5 wt.% Ce_2O_3, and metal fluorides (MgF_2, BaF_2) synthesized by the radiation method were used for research [1]. It should be noted that the samples of oxide ceramics obtained by radiation synthesis, unlike monocrystalline samples, are mechanically fragile glassy formations. Whereas the strength of fluoride ceramic samples is significantly higher and comparable to monocrystalline samples.

CL of the samples was excited by an electron beam with a duration $t_{1/2}$ = 10 ns, an average electron energy in a pulse of 250 keV and an energy density of 0.05 J/cm^2. Measurements of the spectral and kinetic

characteristics of CL were carried out using an MDR-3 monochromator, a FEU-106 photomultiplier and a LECROY WR6030A oscilloscope with a time resolution of 7 ns.

Results and Discussion

1. Spectra and kinetics of Ga_2O_3 CL

The spectrum of Ga_2O_3 CL, recorded at the time of the maximum of the luminescence flash, is represented by a wide band in the region of 2.5 — 4 eV with a maximum of about 3.4 eV. Figure 1 shows the spectrum taken at the moment of the maximum luminescence pulse and 200 ns after. The type of the CL decay curve at 3.44 eV is shown in Figure 2. It can be seen that the decay of Ga_2O_3 CL occurs according to a non-elementary law. The curve has a fast exponential component with a characteristic decay time of 40 ns, as well as a slow hyperbolic one:

$$\mathrm{I(t)} = \frac{0{,}83}{(1+2{,}8\mathrm{t})^2} + 1{,}35 \cdot \exp\left(-\frac{\mathrm{t}}{0{,}04}\right) I(t) = \frac{0{,}83}{(1+2{,}7t)^2} + 1{,}35 \cdot \exp\left(-\frac{t}{0{,}04}\right), \quad (1)$$

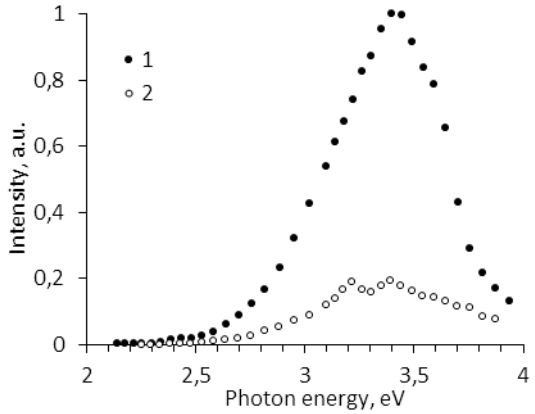

Figure 1. CL spectrum of Ga_2O_3 sample: 1 — taken at amplitude value of a pulse, 2 — in 200 ns.

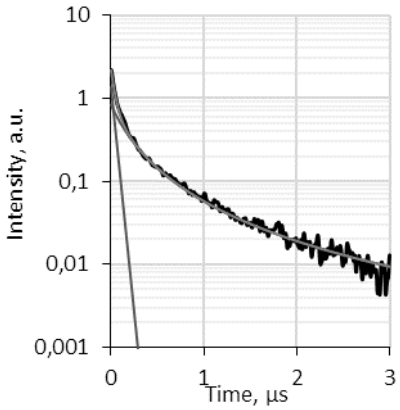

Figure 2. Decay curve of Ga_2O_3 CL at 3.44 eV.

The spectrum of the fast component obtained from the total spectrum (Fig. 3) can be decomposed into two Gaussian bands peaking at 3.05 and 3.45 eV with a width of 0.47 eV. Bands similar in position were observed by the authors of [3] in single crystals of β-Ga_2O_3 under continuous electron irradiation and were associated with the luminescence of point defects.

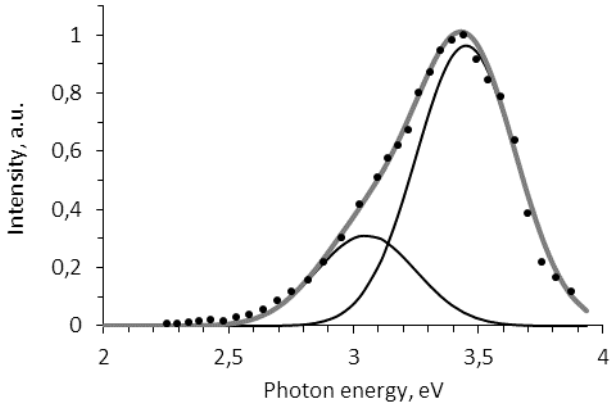

Figure 3. Spectrum of a fast component of Ga_2O_3 CL decay.
Dots — experimental data, solid lines — fitting by Gaussian curves.

2. Spectra and kinetics of Al_2O_3 CL

As for the Al_2O_3 ceramic samples, their spectral and kinetic parameters are difficult to reconcile with the data on single crystals. During the study, we measured the CL spectra of Al_2O_3 and Al_2O_3: Ce 0.5 % samples in the range of 1.3 — 5.3 eV. As can be seen from the data in Figure 4, the most intense glow is observed in the UV region and represents a wide band. Elementary bands with peaks at about 5 eV and 4.3 eV can be distinguished in it, and in samples with an admixture of Ce_2O_3, an additional band appears at 3.4 eV. The band at 4.3 eV was previously observed during irradiation of α-Al_2O_3 with heavy ions [4], but its nature has not been clearly determined. It has been suggested that diffusion-controlled tunnel recombination of self-trapped hole is possible.

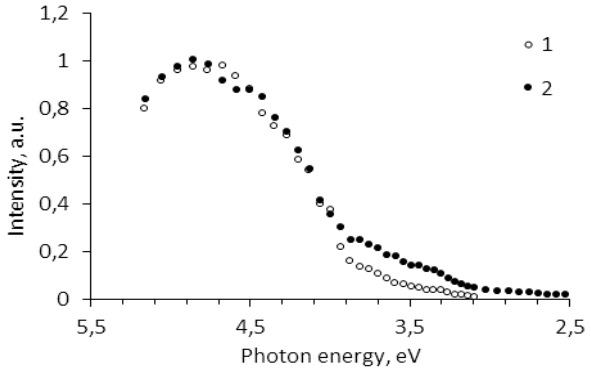

Figure 4. CL spectra of Al_2O_3 (1) and Al_2O_3: Ce 0,5 % (2) samples.

3. Spectra and kinetics of Y_2O_3 CL

The spectral and kinetic characteristics of Y_2O_3 and Y_2O_3 with the addition of 0.5 wt % Ce_2O_3 CL were measured. In general, their spectra, registered by the amplitude values of the flash, are similar (see Figures 5 and 6) and represent a wide band in the region of 2.5 — 4.5 eV, however, the glow of Y_2O_3 with cerium decays much faster. By the time 500 ns after the maximum of the CL pulse, the intensity values are so small that they could not be registered (Figю 6, curve 2). The spectra of the slow and fast decay components of the Y_2O_3 sample CL can be described well by bands with parameters E_{max} = 2.92 eV, FWHM = 0.86 eV and E_{max} = 3.5 eV, FWHM = 0.89 eV, respectively. In the CL spectrum of the Y_2O_3: Ce sample there is only a band at 3.5 eV with FWHM = 0.89 eV.

It should also be noted that the intensity of the emission of the sample containing cerium was more than 10 times lower than that of the sample without cerium. That is, the doping of Y_2O_3 with cerium led to a general decrease in the yield of CL and a decrease in the contribution of relatively long processes associated with the conversion of excitation energy.

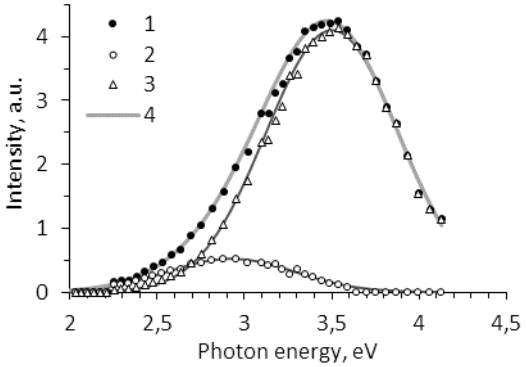

Figure 5. CL spectra of Y_2O_3. 1 — taken by amplitude values of a pulse, 2 — in 500 ns, 3 — spectrum of a fast component, 4 — fitting by a sum of Gaussian curves.

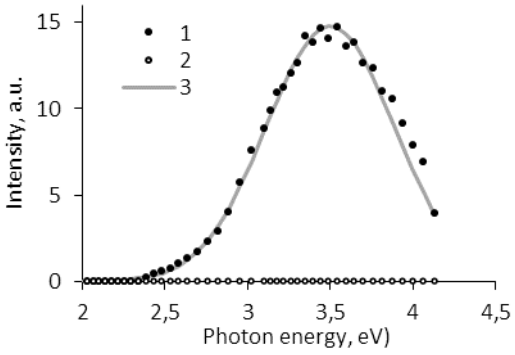

Figure 6. CL spectra of Y_2O_3: Ce 0,5 %. 1 — taken by amplitude values of a pulse, 2 — in 500 ns, 3 — fitting by a Gaussian curve.

4. Spectra and kinetics of MgF_2 u BaF_2 CL

Figure 7 shows the results of MgF_2 and BaF_2 ceramic samples CL spectra measurement. In the MgF_2 spectrum, registered in the 2–4 eV region by peak values of CL pulse, a band at 3 eV with a width of 0.33 eV prevails, in the BaF_2 spectrum in the 2–5 eV region, a band at 4.2 eV with a width of 0.86 eV stands out. The shape and position of the spectra are in good agreement with the data of [5], the authors of which associate these bands with the radiative recombination of self-trapped excitons.

Thus, unlike oxide ceramics, the spectral characteristics of MgF_2 and BaF_2 ceramic samples show good agreement with the data on single crystals of these compounds. This suggests that in compounds with an ionic bond, regardless of their structure (ceramics or single crystal), the short-range order is largely preserved and similar centers of luminescence are formed.

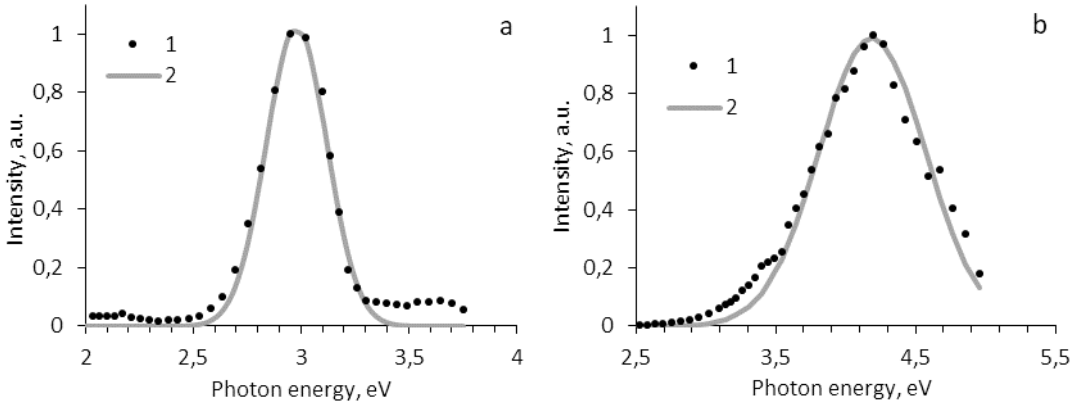

Figure 7. CL spectra of MgF_2 (a) and BaF_2 (б) samples. 1 — experimental data, 2 — fitting.

Conclusions

The study of the spectral and kinetic patterns of the CL of ceramic samples of metal oxides and fluorides obtained by radiation synthesis showed that all studied compounds have a maximum of the CL spectrum in the range of 3–5 eV. Decay of Ga_2O_3 CL occurs according to a non-elementary law. There is a fast exponential component and a slow hyperbolic one in the pulse. Moreover, the spectrum of the fast component can be decomposed into two bands (3.05 and 3.45 eV) close in position to those observed by the authors of [3] in single crystals of β-Ga_2O_3 under continuous electron irradiation and associated with the luminescence of point defects.

In the spectra of Al_2O_3 CL, elementary bands with maxima at 5 eV and 4.3 eV can be distinguished, and in samples doped with Ce_2O_3 an additional peak at 3.4 eV, which was observed earlier when irradiated with α- Al_2O_3 with heavy ions. Its origin has not been definitively determined.

The spectra of Y_2O_3 CL without and with a dopant of Ce_2O_3 are similar, but the luminescence of Y_2O_3: Ce decays much faster and the intensity of this emission is significantly reduced. That is, the introduction of cerium into Y_2O_3 leads to an overall decrease in the yield of CL and a decrease in the contribution of relatively long processes associated with the conversion of excitation energy.

The spectra of MgF_2 and BaF_2 ceramic samples show good agreement with the data on single crystals of these compounds, unlike oxide ceramics. This indicates that in compounds with an ionic bond, regardless of their structure (ceramics or single crystal), the short-range order is largely preserved and similar centers of luminescence are formed.

Acknowledgments

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Жоғары энергиялы электрондар ағыны саласында синтезделген оксидті және фторлы керамиканың катодолюминесценция қасиеттері

Дәстүр бойынша отқа төзімді керамиканың синтезі күрделі және көп уақытты қажет ететін процесс. Біраз уақыт бұрын жаңа, әлдеқайда жылдам әдіс — жоғары энергиялы электрондардың қуатты ағыны саласындағы люминесцентті керамиканы синтездеу әдісі ұсынылды. Көп компонентті оксидті фосфорларды синтездеу кезінде алынған материалдың қасиеттерінің шикізат қоспасының құрамына және синтез процесінің режимдеріне тәуелділігін анықтау оңай шаруа емес. Осыған байланысты күрделі фосфорлардың құрамдас бөліктері болып табылатын қарапайым оксидтерден радиациялық синтез арқылы жасалған керамиканың қасиеттерін зерттеу қисынды болып көрінеді. Жұмыста радиациялық синтез әдісімен алынған металл оксидтерінің (Ga_2O_3, Al_2O_3, Y_2O_3) және фторидтердің (MgF_2, BaF_2) керамикалық үлгілерінің катодолюминесценциясының спектрлік және кинетикалық заңдылықтарына зерттеу жүргізілді. Люминесценция импульсі 250 кэВ болатын электрондардың орташа энергиясы бар электрондар шоғырымен қозғалды. Спектрлер мен люминесценция кинетикасын тіркеу үшін 7 нс уақыт ажыратымдылығы бар импульстік спектрометрия әдісі қолданылды. Авторлар зерттелген үлгілердің катодолюминесценция спектрлеріне қарапайым жолақтарды бөліп көрсете отырып, жеке жолақтардағы люминесценцияның әлсіреу динамикасы туралы қорытынды жасайды. Алынған нәтижелерді монокристалды үлгілер бойынша белгілі деректермен салыстыру жүргізілді. Оксидті керамикадан айырмашылығы, MgF_2 және BaF_2 керамикалық үлгілерінің спектрлік сипаттамалары осы қосылыстардың монокристалдары туралы мәліметтермен жақсы үйлесетіндігін көрсетеді.

Кілт сөздер: оксидті керамика, фторлы керамика, катодолюминесценция, радиациялы синтез, спектрлер, уақыт ажыратымдылығы, Ga_2O_3, Al_2O_3, Y_2O_3.

А.А. Карнаухова, В.Ю. Яковлев

Свойства катодолюминесценции оксидной и фторидной керамики, синтезированной в поле потока высокоэнергетических электронов

Традиционно синтез тугоплавкой керамики является сложным и долгим процессом. Некоторое время назад был предложен новый, намного более быстрый метод — метод синтеза люминесцентной керамики в поле мощного потока высокоэнергетических электронов. Синтез оксидной керамики по принципиально новой технологии требует всестороннего изучения свойств этой керамики. При синтезе многокомпонентных оксидных люминофоров непростой задачей является определение зависимостей свойств получаемого материала от состава исходного сырья, режимов процесса синтеза. Образцы для данной работы были синтезированы путем прямого воздействия на сырье электронного пучка. В работе исследовались закономерности катодолюминесценции образцов керамики оксидов металлов (Ga_2O_3, Al_2O_3, Y_2O_3) и фторидов металлов (MgF_2, BaF_2), синтезированной радиационным методом. Люминесценция возбуждалась пучком электронов со средней энергией электронов в импульсе 250 кэВ. Для регистрации спектров и кинетик люминесценции использовался метод импульсной спектрометрии с временным разрешением 7 нс. Авторами представлен анализ спектров катодолюминесценции изученных образцов с выделением элементарных полос, сделаны заключения о динамике затухания люминесценции в отдельных полосах. Проведено сравнение полученных результатов с известны-

ми данными по монокристаллическим образцам. Показано, что, в отличие от оксидной керамики, спектральные характеристики образцов керамик MgF_2, BaF_2 показывают хорошее соответствие с данными по монокристаллам этих соединений.

Ключевые слова: оксидная керамика, фторидная керамика, катодолюминесценция, радиационный синтез, спектры, временное разрешение, Ga_2O_3, Al_2O_3, Y_2O_3.

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