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Crystal phosphors for storage luminescent screens

A M Gurvich, V V Mikhailin
Scientific-Research X-Ray Radiological Institute, Moscow
M V Lomonosov State University, Moscow

ABSTRACT. A review is given of the work on photostimulated crystal phosphors as materials of storage luminescent screens used in digital radiography. The properties of barium fluorohalides, particularly of BaFBr:Eu, important in these applications are considered. Much attention is given to the influence of conditions during preparation on these properties, to physicochemical relationships describing the processes of formation and interaction of crystal lattice defects, and to the current ideas on the mechanism of photostimulated luminescence.

The bibliography contains 94 references.

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I. Introduction. Storage luminescent screens as alternatives to silver-halide photographic materials

Inorganic (crystal) phosphors, storing energy and liberating it in the form of light—photostimulated luminescence excited by infrared or visible radiation—have been known for a long time. They are used in dosimetry and in visualisation of infrared radiation.[1–4] The development of computers and lasers has opened up new opportunities for the applications of these materials and this has led to the development of luminescent digital (computer) radiography.[5,6] This method differs from conventional radiography because instead of a photographic (radiographic) film or its combination with amplifying screens, use is made of an image-storing crystal phosphor (we shall use just the word phosphor) screen capable of emitting luminescence.

The latent image is developed by scanning such a screen with a sharply focused beam of a helium–neon laser. The light flashes (scintillations) generated are converted in a photomultiplier into a series of electrical signals and then, after discretisation, they are made up into a digital code. The data digitalised in this way are stored in an optical disk or on a magnetic tape, and—after computer processing—are converted back into analog signals, modulating the intensity of an electron beam used in a display or modulating radiation from a second laser which scans a photographic film†.

Luminescent digital radiography has a number of advantages over conventional (film) radiography,[7] the main of these is a wide dynamic range.[8,9] This makes it possible, for example, to attain a high-contrast resolution of parts of an object which differ greatly in respect of the absorption of ionising radiation, and also to reduce the risk of obtaining a poor-quality image because of an incorrect selection of the exposure conditions.

The idea of luminescent digital radiography has long been in the "air" (see, for example, Ref. 10), but it has been realised only after the development of phosphors satisfying the full range of the necessary requirements.

II. Selection of crystal phosphors for storage screens

Phosphors used in luminescent screens should satisfy the following requirements:[7,11] 1) a high energy efficiency of the room-temperature photostimulated luminescence in order to reduce the noise associated with fluctuations of the photon flux; 2) luminescence and excitation bands sufficiently far apart for spectral separation of the laser radiation from the photostimulated luminescence; 3) a rapid decay of the laser-excited light flashes, so as to ensure the necessary speed of image readout (reconstruction) and prevent superposition of signals due to different parts of the image; 4) long-term retention of the stored energy (weak fading); 5) a linear dependence of the photostimulated luminescence intensity on the exciting-radiation dose, which is the precondition for the attainment of a wide dynamic range; 6) efficient absorption of ionizing radiation in order to minimize the quantum noise and reduce the dose necessary to obtain a high-quality image.

These requirements were taken as the basis of an investigation of the feasibility of using a large number of phosphors capable of the photostimulated luminescence. These phosphors included zinc and alkaline-earth sulphides, for example SrS:Ce:Sm and SrS:Eu:Sm;[1,17] alkali halides,[10,13] particularly RbBr:Tl;[9,11] oxides (ThO_2:Er) and oxysulphides (La_2O_2S:Eu:Sm);[12] alkaline-earth fluorohalides;[5,14] some sulphates, borates, and silicates;[11,13,15] haloborates, halosilicates, halophosphates, and halogermanates of alkaline-earth metals, particularly $Ba_5SiO_4Br_6$:Eu.[11,16] In the case of luminescent digital radiography the best of these phosphors have proved to be barium fluorohalides activated with europium (BaFHal:Eu), the ability of which to emit the photostimulated luminescence had been investigated early,[5,14] as well as later on a large number of occasions. A particularly favourable combination

† In the latest systems made by Fuji the same laser is used to scan a storage screen and a photographic film.

of properties is exhibited by the BaFBr:Eu phosphor,[12,17–19] used in storage screens manufactured on a commercial scale.[17] The energy efficiency of its photostimulated luminescence can reach 5%[19] and the luminescence (λ_{max} = 390 nm) and excitation (λ_{max} = 590–600 nm) bands are far apart, the photostimulated luminescence decay time is τ = 0.8 μs,[8] the fading does not exceed 25% in 8 h,[17] and the presence of barium in the phosphor base ensures a strong absorption of X-rays.[20] It should be pointed out that unsuccessful attempts had been made and are still being made to improve some properties of BaFBr:Eu by partial replacement of Br with Cl or I.[13]

III. Structure and principal properties of barium fluorohalides

The first barium fluorohalide to attract attention was BaFCl as an object of investigations of colour centres[21–24] and (when activated with europium) as an efficient phosphor for amplifying X-ray screens.[25,26] The high efficiency of the photoluminescence and cathodoluminescence of MFHal:Eu^{2+} phosphors (M = Sr, Ba; Hal = Cl, Br) was mentioned in Ref. 27.

Barium and strontium fluorohalides have a layer tetragonal structure of the PbFCl type,[28,29] which can be represented by a sequence of layers F_2MHalHalM..., oriented along the [001] direction (Fig. 1). The subscript 2 of fluorine indicates that the number of ions in an F^- layer is twice as high as in Hal or M layers. The distances between the F^- ions are $\sqrt{2}$ times less than the distances between the Br^- and Ba^{2+} in the relevant layers.

The presence of anions of two types in barium fluorohalide crystals facilitates the formation of two different types of the colour (F) centres, for example, fluorine‡ (V_F) and chlorine (V_{Cl}) vacancies in BaFCl, and of fluorine and bromine (V_{Br}) vacancies in BaFBr, when these vacancies have captured electrons. The appearance of the corresponding bands in the absorption spectra of crystals had been confirmed experimentally, and an investigation of the ESR spectrum[22] and a theoretical analysis[23] have resulted in an attribution of the short-wavelength band to the V_F centres, which are frequently denoted also by the symbol $F(F^-)$. It has also been shown that additive colouring produces only the F centres of the V_F type.[30] This can be explained by the fact that an excess of Ba penetrates deeper into crystals along dislocations, which are formed at the edge between two adjacent F_2 and Ba layers that terminate inside the crystal (at the edges of BrBrBa layers the formation of dislocations is less probable for steric reasons).

We investigated earlier[14] the characteristics of the luminescence emitted by the $BaCl_2-BaF_2$ system and showed that an excess of BaF_2 formed a solid solution in BaFCl. This implied that some of the Cl^- ions were replaced with F^- giving rise to antisite defects F_{Cl}.[19] The presence of similar defects was postulated also for BaFBr.[33] The association of these defects§ with $V_{Cl}^{\cdot}$ ($V_{Br}^{\cdot}$) gave rise to F centres with parameters differing somewhat from those of non-associated centres of this type.[19]

‡The subscript of the symbol for a defect identifies the lattice sites at which this defect is formed or an interstitial position (i), as is usual in the literature on the physical chemistry of solids.[31,32]

§Here and later a dot (bullet) is used to denote an effective positive charge of a defect relative to the surrounding lattice and a prime is used for an effective negative charge (the number of the primes indicates the magnitude of the charge).

Barium fluorohalides are capable of emitting luminescence unrelated to the presence of impurities. As in the case of other halide phosphors,[34] it can be explained by the recombination of electrons with V_k centres (molecular Hal_2 centres, formed by the capture of a hole shared by two adjacent halogen ions).[35,36] The presence of two different halogens in a crystal facilitates the formation of at least two types of V_k centres, for example F_2^- and Cl_2^- in BaFCl. The F_2^- ions are taken to be responsible for a short-wavelength luminescence band observed only at low temperatures for all the fluorohalides and for BaF_2.[35] The room-temperature luminescence of nonactivated BaFCl and BaFBr has been attributed to the recombination of electrons with the Cl_2^- and Br_2^- centres, respectively. They are formed by Hal^- ions located at the shortest distance from one another in adjacent layers. In view of the lower electronegativity of Br, compared with Cl, it is found that the V_k centres of the Br_2^- type predominate in mixed $BaFCl_xBr_{1-x}$ crystals.[35] The presence of V''_{Ba} barium vacancies may have a stabilising influence on the adjoining V_k centres.

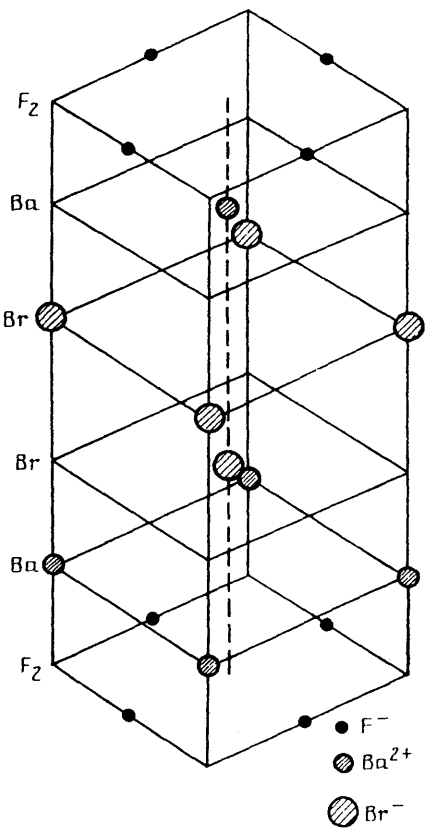


Figure 1. Positions of ions in the crystal lattice of BaFBr. The symbols F_2, Ba, and Br identify the layers formed by the F^-, Ba^{2+}, and Br^- ions, respectively.

Barium and strontium fluorohalides are readily activated by divalent rare-earth ions such as Eu^{2+} [5,25,37,38] and Sm^{2+},[39,40] because such activation does not require charge compensation. The

luminescence spectrum of Eu^{2+}, characterised by a strong room-temperature band with a maximum at 385 nm for BaFCl and at 390 nm for BaFBr, is very suitable for luminescent digital radiography, because this spectrum corresponds to the maximum sensitivity region of ordinary photocathodes and at the same time is shifted significantly relative to the excitation bands,[5] as demonstrated in Fig. 2 using the example¶ of BaFBr : 10^{-4} Eu.[41]

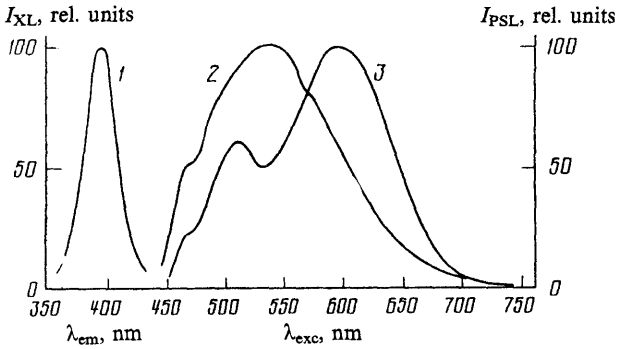


Figure 2. The luminescence (*1*) and excitation (*2*, *3*) spectra of BaFBr : 10^{-4} Eu phosphor prepared by heating a charge at 800 °C without further annealing (*2*) and after annealing at 550 °C (*3*). The spectra were recorded at 20 °C. The abscissa gives the wavelengths of the emitted luminescence (λ_{em}) and of the exciting (λ_{exc}) light and the ordinate gives the intensities of the X-ray luminescence (I_{XL}) and of the photostimulated luminescence (I_{PSL}). The spectra distribution of the photostimulated luminescence of BaFBr : Eu phosphor is identical with its X-ray luminescence spectrum. The curves are normalised to the maximum.[41]

In addition to the luminescence band due to the $4f^6 5d \rightarrow 4f^7$ transition in the Eu^{2+} ion, there may be a line 363 nm due to the $4f^7 \rightarrow 4f^7 ({}^6P_{7/2} \rightarrow {}^8S_{7/2})$ transition.[37] This transition becomes possible because, due to the relatively weak splitting of the 5*d* state into ^2e_g and $^2t_{2g}$, the lowest excited 4*f* level lies somewhat below the ^2e_g levels. The line at 363 nm becomes weaker, compared with the above-mentioend luminescence band, when Sr is replaced with Ba and when Cl is replaced with Br or I, and it also becomes weaker with increase in temperature,[37] so that in the case of BaFBr : Eu and BaFI : Eu this band is no longer observed at room temperature.

When the BaFCl : Eu phosphor is used in the preparation of amplifying screens, one of the most difficult tasks is to suppress a weak but very persistent afterglow,[26,38,42] indicating the presence of deep traps. It is an investigation of this effect, manifested more clearly in the case of BaFBr : Eu,[25] that has led to the discovery of the ability of fluorohalides to store a large amount of light energy and to liberate this as a result of optical stimulation. Charge separation, which is the condition for storing the energy, is due to a strong capture of holes by the Eu^{2+} centres and of electrons by the anion vacancies. The participation of the $V_F^{\cdot}$ and $V_{Hal}^{\cdot}$ in this process is confirmed by a comparison of the stimulation and absorption spectra of the *F* centres, which are formed by the capture of electrons.[43] The energy efficiency of the photostimulated luminescence of BaFBr : Eu excited by X-ray radiation can reach 5%.[19] Moreover, a rapid decay of the photostimulated luminescence flashes is important: it is due to the fact that the rate-limiting stage of the process is the allowed intracentre $4f^6 5d \rightarrow 4f^7$ transition. In the case of continuous optical stimulation, the rate of emptying of traps τ_{em}^{-1} is proportional to the maximum photostimulated luminescence intensity I_{PSL}, which in turn is governed by the intensity of the exciting (stimulating) light I_{st} and by the initial concentration of electrons n_F captured by the *F* centres:

$$I_{PSL} = \sigma I_{st} n_F. \qquad (1)$$

Here, τ_{em} is the time during which the photostimulated luminescence intensity decreases by a factor *e* under the conditions of continuous excitation and σ is the cross section of the optical excitation process.[44]

IV. Dependences of properties of BaFBr : Eu phosphor on the conditions during its preparation

Among the many known methods for the preparation of barium fluorohalides,[20,25,29,45] three have been found suitable for the preparation of BaFBr : Eu phosphors. One of them, mentioned in the majority of the investigations (see, for example, Refs. 12, 18, and 44), is a solid-phase reaction involving heating of a charge composed of a mixture of BaF_2 and $BaBr_2$, containing europium bromide[12] or fluoride.[42] The second method differs from the first because the initial stage of the process occurs in an aqueous suspension of fine grained BaF_2 in a solution of $BaBr_2$.[25,46,47] After evaporation of the suspension and addition of $EuBr_3$, the resultant charge is heated usually in a reducing atmosphere. A special feature of the third method is that the source of fluorine is NH_4F,[19,41,48,49] interacting with $BaBr_2$ first in the solution and then (after evaporation) in the solid phase.

The properties of BaFBr : Eu depend very strongly on the conditions during its preparation.[10,41,50,51] The highest photostimulated luminescence efficiency is usually obtained when the concentration of europium is less than that needed to ensure the strongest steady-state luminescence.[41] If NH_4F is used as a fluorinating agent, this concentration is almost an order of magnitude less than for the interaction of $BaBr_2$ with BaF_2, and it amounts to 10^{-4} g-atom/mol.[52] The fluorinating effect of NH_4F favours also the incorporation of other rare-earth activators in the lattice and removal of oxygen† from it, which increases the phosphorescence intensity and reduces the photostimulated luminescence intensity, obviously due to the formation of defects of the $O'_{Br}V_{Br}^{\cdot}$ type.[19] Although the activation of BaFBr by divalent europium is quite efficient when a charge is heated together with NH_4F and with a flux (the flux may be, for example, KBr—see Ref. 41) in air, it is preferable to use a weakly reducing medium such as nitrogen containing an admixture of hydrogen[12,44] or of CO.[19,26,53] Even in this case we cannot prevent the formation of the

¶ The number in front of the activator symbol is its concentration in gramme-atoms per mole in the charge from which the phosphor was prepared.

† The source of oxygen can be water of crystallisation with which barium halides readily interact.[21]

O'_{Hal} centres.[54] The nature of the flux has a considerable influence on the excitation spectrum[52] and its concentration—and the temperature to which it is heated—affects the grain size.[45] In selecting the method for removal of the flux we must bear in mind that the hygroscopic nature of MFHal compounds and their tendency to hydrolyse increases on reduction in the size of the M^{2+} cation and on increase in the size of the Hal^- anion;[29] in the case of BaFBr it is considerably greater than in BaFCl.

An important aspect is the choice of the temperature at which a charge is heated[41] and of the ratio of the components forming the base of a phosphor. This ratio influences the completeness of the solid-phase reaction,[29,57] as well as the excitation spectrum and fading.[12] The changes in the properties of BaFBr:Eu with the rate of its cooling and the conditions during annealing are particularly striking.[41,55,56] It is found that if the excess of $BaBr_2$ is reduced before annealing,[52] the subsequent annealing of the phosphor at 450–650 °C shifts the maximum in the excitation spectrum (Fig. 2) from the yellow–green region (520–540 nm) and orange–red (595–600 nm). This reduces the intensity of the steady-state X-ray luminescence, weakens greatly the room-temperature phosphorescence, and lowers the total light (liberated due to thermal excitation) by at least an order of magnitude; the high-temperature peaks on the thermoluminescence curve are much stronger than the low-temperature peaks. On the other hand, the photostimulated luminescence efficiency sometimes even rises. The determination of the excitation spectra at liquid nitrogen temperature during the subsequent annealing of the thermally stimulated luminescence (thermoluminescence) peaks provides additional support for the conclusion that there is no direct relationship between the characteristics of thermally and optically stimulated luminescence.[41] This follows from the fact that optical de-excitation of the investigated phosphor does not suppress the thermoluminescence or phosphorescence.[50,52]

V. Crystal lattice defects in BaFBr:Eu phosphor and photostimulated luminescence mechanism

If we assume that thermal disordering of the BaFBr lattice can produce both the Frenkel and the Schottky defects, and that the antisite defects can also be present, we have to allow for the formation of the following point defects in BaFBr:Eu phosphors:[19,33,57,58] V''_{Ba}, $V_{\dot F}$, $V_{\dot{B}r}$, F'_i, Br'_i, F_{Br}, and Eu_{Ba}. Computer modelling of defects in crystals[59] has made it possible to calculate the enthalpy and entropy of the processes of disordering of the BaFBr lattice.[33] A thermodynamic analysis based on these data shows[58] that among the effectively charged point defects in a regular lattice at the temperatures of formation and annealing of these phosphors the $V_{\dot{B}r}$ and F'_i defects shoud predominate (at 550 °C their concentration should be an order of magnitude less than at 800 °C). The following approximate equation corresponds to equilibrium:

$$[F'_i] \approx [V^*_{\dot{B}r}]. \qquad (2)$$

A comparison of the excitation spectra with the action spectra for attenuation of the ESR signal under the influence of exciting light[8] leads to the conclusion that the vacancies $V_{\dot{B}r}$ are responsible only for the long-wavelength part of the excitation spectrum with its maximum at 595–600 nm, whereas the short-wavelength region, which predominates in the case of the nonannealed phosphor (Fig. 2), is associated with $V_{\dot F}$.

This apparent disagreement between the theoretical calculations and experiments is removed if we allow for the data on the influence of annealing BaFBr:Eu given in the preceding section on the thermally stimulated luminescence and the photostimulated luminescence.[41,58] Obviously, annealing (like slow cooling) in the preparation of ZnS:Cu electroluminescent phosphors[32,60] results in segregation of point defects, so that they concentrate near dislocations and block boundaries. As pointed out already (see Section III), dislocations are more likely to form at the edges between two adjacent F_2 and Ba layers. Such dislocations can generate $V_{\dot F}$ and V''_{Ba}) vacancies, but these remain in the region of a crystal adjoining an extended defect. Annealing a phosphor causes the $V_{\dot{B}r}$ vacancies, which predominate in the bulk of a crystal, as well as interstititial F'_i ions and the Eu_{Ba} impurity defects to migrate towards dislocations and block boundaries. This process is accompanied by the interaction of F_i with $V_{\dot F}$,

$$F'_i + V^*_F = F_F, \qquad (3)$$

which increases the concentration ratio $[V_{\dot{B}r}]/[V_{\dot F}]$. If we now assume that the photostimulated luminescence is generated mainly near linear and surface defects, whereas the thermally stimulated luminescence is primarily due to the processes that occur in a regular lattice, we can account for all the reported data on the influence of annealing: the enhancement of the photostimulated luminescence in the long-wavelength part of the excitation spectrum, which corresponds to $V_{\dot{B}r}$, the absence of a direct relationship between the thermally stimulated luminescence, which is weakened by annealing, and the photoluminescence which is then even enhanced, as well as the reduction in the afterglow and in the energy efficiency of steady-stage luminescence caused by annealing. Moreover, we can also account for the results of a number of investigations supporting the tunnel mechanism of the photostimulated luminescence. These include a weak temperature dependence of the decay time of the photostimulated luminescence when excitation is in the form of short light pulses[18] (this is also true of KI:Tl-type phosphors[10]) and the absence of photoconductivity when excitation occurs under conditions such that the photostimulated luminescence is generated with the participation of effectively only the V_F centres.[61] From this point of view, the possibility of tunnel transitions of electrons is the result of the following: segregation of point defects near linear and surface defects brings close together the luminescence centres (Eu_{Ba}) and the anion vacancies.[41] The fact that the photostimulated luminescence involving the V_{Br} centres is accompanied by photoconductivity, whose excitation spectrum is similar to the luminescence excitation spectrum,[43,61] should be regarded as evidence of the coexistence of the tunnel mechanism of optical excitation with photostimulated luminescence occurring due to transitions of electrons via the conduction band,[41] although the former mechanism clearly predominates. On the other hand, the thermally stimulated luminescence and the room-temperature phosphorescence are emitted in all cases with involvement of the conduction band and are primarily due to defects located in the regular lattice.

In the course of determination of the excitation spectra of BaFBr:Eu phosphors at liquid nitrogen temperature, following successive annealing of the thermally stimulated luminescence peaks, it has been established that such annealing increases considerably the energy efficiency of the photostimulated luminescence and the contribution of the short-wavelength components in the excitation spectrum.[41] This can be explained by the transfer of electrons from traps, responsible mainly for the thermally stimulated luminescence, to traps which are the most active in the photostimulated

luminescence process. Exactly the same explanation has been applied to the partial recovery of the photostimulated luminescence after complete optical de-excitation of a phosphor.[52] The kinetics of this process, described by the equation

$$I_{PSL} = k\sqrt{t} \quad (4)$$

(where t is the storage time of a phosphor after the de-excitation and k is a coefficient), is evidence of the diffusive nature of the transfer of electrons. It should be pointed out that a model allowing for the tunnel mechanism of the photostimulated luminescence and based on the hypothesis of radiative formation of the F centres as a result of formation of $F-H$ pairs on decay of excitons located near activators[18,36] fails to account for all the observations, particularly for the strong influence of the conditions during cooling and annealing of a phosphor on the excitation spectrum and on the photostimulated luminescence energy efficiency.

A careful investigation of the excitation spectrum reveals its complex structure, which cannot be reduced to the presence of two bands.[19,41] This can be explained by the fact that the F-centres governing the form of the spectrum differ from one another not only by the nature of the anion vacancy (V_F, V_{Br}), but also in respect of its environment, particularly because of the already mentioned association with other defects, primarily with antisite defects of the F_{Br} type.[19,62] Some role may be played here also by the distribution of the excited p-state of the F-centres.[22,63]

In investigations of phosphors based on BaFCl and activated with Eu^{2+} and Sm^{2+} it has been found that their properties change greatly, and the changes include enhancement of the phosphorescence, in the presence of an excess of BaF_2.[38,39,45] There are indications that an excess of BaF_2 influences also the properties of BaFBr:Eu by increasing the proportion of the bands associated with V_{Br} in the excitation spectrum.[12] This can be attributed to intercrystalline reactions of the type

$$F_{Br} = V^{*}_{Br} + F'_i, \quad (5)$$

$$F_{Br} + V^{*}_{F} = F_F + V^{*}_{Br}. \quad (6)$$

The first of these can be called the antisite Frenkel disordering.[52] It obviously plays a specially important role, because it involves participation of the V_{Br} and F'_i defects which dominate in the regular lattice. It therefore follows that it is necessary to control rigorously the conditions during preparation, which influence the excess of BaF_2, particularly during the stage of washing away the flux and annealing of BaFBr:Eu phosphors[52,64] (hydrolysis during washing of BaFBr can remove a certain amount of $BaBr_2$).

VI. Excitation spectra of steady-state luminescence, phosphorescence, and photostimulated luminescence of barium fluorohalides

The excitation spectra of steady-state luminescence, phosphorescence and photostimulated luminescence of barium and strontium fluorohalides, which are of interest from the purely scientific and utilitarian points of view, had been investigated in a wide range of energies on a number of occasions.[14,36,38–40,50,64–70] The long-wavelength edge of the main (strongest) band in the excitation spectrum of the phosphorescence, which is obviously associated with interband transitions, has been used to estimate the band gap E_g of BaFCl.[14] This band gap is 8.5–9 eV. The corresponding band gap of BaFBr is 8–8.5 eV.[40,43,71]

In the range $E < E_g$ the excitation spectra of the steady-state luminescence depend on the nature of the luminescence centres and, therefore, they are different for nonactivated phosphors and for phosphors containing Eu^{2+} and Sm^{2+}.[39,40] They depend at least in the case of activation with europium, also on the oxidation—reduction properties of the medium in which a phosphor is heated during preparation.[38] For example, the excitation spectrum of BaFCl:2×10^{-2} Eu, prepared in a CO medium, includes a strong activator band extending from 3.3 to 5.4 eV with a barely detectable splitting into two bands due to the $5d(^2e_g)$ and $5d(^2t_{2g})$ states of the Eu^{2+} ion. Howevever, heating of this phosphor in air at 650–700 °C weakens strongly the Eu^{2+} band (although the intensity of the steady-state X-ray luminescence even rises somewhat[26]). Then, a weak peak at 318 nm remains in the long-wavelength part of the excitation band whereas a structure appears in the short-wavelength part corresponding to the t_{2g} state and this structure is due to transitions of electrons from the $4f^7(^8S)$ level to the levels of the $4f^6(^7F_J)5d(^2t_{2g})$ state split by the spin–orbit interaction. Heating in CO smears out this structure because of reduction of europium on the phosphor surface, where the Eu^{2+} ions may be in a different environment.[38] The structure of the part of the spectrum located between the band corresponding to the intracentre transitions and the energy E_g is attributed to the ionisation of Eu^{2+} and the presence of the edge Γ excitons [at 8.4 eV in the case of BaFCl and at 7.4 and 7.9 eV in the case of BaFBr [39,66,71]] associated with the $4p$-states of the Cl^- and Br^- ions.

The nature of the excitation spectra of the steady-state luminescence recorded in the range $E > E_g$ is practically independent of the activator and there is a considerable qualitative similarity of the BaFCl and BaFBr spectra (Fig. 3). The most remarkable feature of the spectra in the range 9–30 eV is the presence of a two-hump maximum at 16–20 eV in the case of BaFCl and 15–19.5 eV in the case of BaFBr. It can be attributed to the simultaneous influence of the formation of a plasmon and a core exciton,[40] due to the excitation of electrons in the $5p$-shell of the Ba^{2+} ions. The formation of an exciton increases the absorption coefficient and thus enhances the surface losses and gives rise to a narrow dip in the spectrum at 18.1–18.3 eV. The photon multiplication is manifested largely by a tendency to establish a constant energy efficiency η of the luminescence rather than by an abrupt increase in the quantum efficiency η_q.[39,40] Already in the range 20–30 eV the value of η becomes approximately equal to the energy efficiency of X-ray luminescence: 11–12% for BaFCl:10^{-2} Eu and 16–18% for BaFBr:Eu.[40,41] In the case of BaFBr:Eu the constancy of η is supported by measurements in the range from 10 to 1000 eV.[70] The annealing of BaFBr:Eu at 550 ± 100 °C reduces the energy efficiency of the steady-state luminescence at $E > 11$ eV by a factor of about 2; on the other hand, at 10 eV a strong excitation band is observed (Fig. 4 *a*) and this band is difficult to detect in the case of nonannealed phosphors. It is possibly due to the formation of F_{Br} clusters (10 eV is the initial energy of the appearance of excitons, bound to the $2p$-states of the F^- ions[36]).

The excitation spectrum of the photostimulated luminescence of BaFBr:Eu had been determined under somewhat different conditions by two research teams independently.[36,50,64–66] We can see from Fig. 4 that in the range $E > 11$ eV this spectrum is basically similar to the excitation spectrum of the steady-state luminescence. On the other hand in the range $E < 11$ eV of the two spectra are very different. For example, at 10 eV instead of a maximum, observed in the excitation spectrum of the steady-state

luminescence of the annealed phosphors, the corresponding photostimulated luminescence spectrum has a dip. A narrow intense peak at 7 eV is very typical of the excitation spectrum of the photostimulated luminescence. Following the two concepts of the mechanism of the photostimulated luminescence mentioned above, this peak is attributed to a transition of an electron from Eu^{2+} to an adjacent vacancy or to an exciton, the dissociation of which forms a $F-H$ pair.[36,50] It is important to stress that the phosphorescence of BaFBr:Eu begins to be excited effectively at higher energies of about 8 eV.[50]

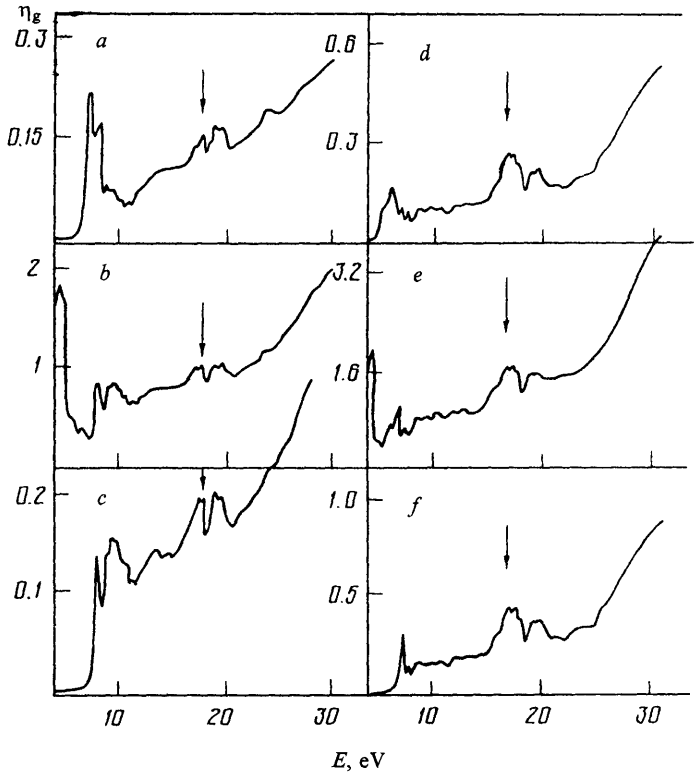


Figure 3. Excitation spectra of steady-state luminescence of non-activated BaFCl (*a*), BaFCl:2×10^{-2}Eu (*b*), BaFCl:10^{-2}Sm (*c*), nonactivated BaFBr (*d*), BaFBr:10^{-3}Eu (*e*), and BaFBr:10^{-2}Sm (*f*). The ordinate represents the quantum efficiency relative to sodium salicylate. The arrows identify the calculated values of the plasmon energy.[40]

VII. Some applications of storage luminescent screens

The development of storage luminescence screens and of the luminescent digital radiography based on them has opened up new opportunities in X-ray diagnostics. This is based on the combination of computer techniques with the large area of the images required in medicine, a relatively high spatial resolution, and a wide dynamic range. There have been several reports on the application of luminescent digital radiography in examination of lungs, breasts, and other organs,[72–77] and in checking the position of a radiation beam as well as in obtaining information on the distribution of the dose in a body being irradiated by radiotherapy.[56,78,79] Technical difficulties and cost are hindering the extension of a wider use of the method in medicine.[7,80]

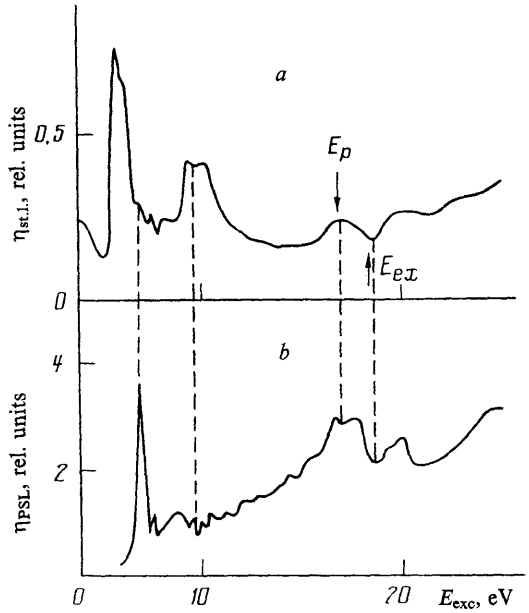


Figure 4. Excitation spectra of the steady-state luminescence (*a*) and of the photostimulated luminescence (*b*) of BaFBr:10^{-4}Eu phosphor annealed at 550 °C. The arrows identify the calculated values of the plasmon energy (E_p) and of the energy of the core exciton (E_{ex}), formed on excitation of electrons from the 5*p*-shell of the Ba^{2-} ion.[50]

There have been several descriptions of the application of luminescent digital radiography in obtaining diffractograms,[81,87] particularly in studies of biological objects with the aid of synchroton radiaiton. This method can be used to obtain high-quality records after exposures tens of times shorter than usual.[81,84,85] There have been suggestions of the use of luminescent digital raidography in transmission electron microscopy[88] and in recording various radiations both electromagnetic—from the VUV range[40,89] to the bremsstrahlung emitted by electron accelerators[56]—and the corpuscular,[89] including determination of the natural background. One should bear in mind that barium salts employed as phosphors usually contain a small amount of radium.[17,20] Obviously, luminescent digital radiography can be used also in astrophysics research, including X-ray astronomy, where a wide dynamic range of energy storing luminescent screens can be particularly valuable.

The different applications of these screens have led to studies of the parameters governing the quality of the images obtained by luminescent digital radiography and of threshold values of the flux

of the radiation being detected.[6,81,90–92] As usual, a dominant role is played by the efficiency of energy conversion of the radiation which excites the emitted luminescence, by the noise, by the frequency–contrast characteristic, by the dynamic range, and by the kinetic parameters.[93] On the other hand, these screen quality factors and systems as a whole are influenced by a number of factors specific to luminescent digital radiography.[7,90] These factors depend on the properties of the phosphors and screens employed and include the scattering of exciting light,[11] fading,[13,94] and fluctuations of photon fluxes (luminescence noise).[87] The last of these factors is particularly important as a component of the general noise in the case of a low energy efficiency of the photostimulated luminescence and high light losses between a screen and a photomultiplier.

We can thus see that the development of efficient crystal phosphors or image-storing screens and of the luminescent digital radiography method based on these screens has laid the foundation stone for a new branch of research, which is now developing rapidly in various directions.

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