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Creation of F centres and multiplication of electronic excitations in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics under VUV irradiation

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Abstract

The reflection spectra, the excitation spectra of various emissions (2.4–4.5 eV) and the creation spectra of F centres have been measured in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical sodalite ceramics ($x = 0.94$ and $x = 0.81$) using VUV radiation of 6–35 eV. An analysis of the spectra allowed us to separate several groups of electronic excitations: the photons of 6.7–8.3 eV excite or ionize Br^- centres in the β -cages, 8.5–32 eV photons generate electronic excitations of the aluminosilicate carcass, while 33 eV photons excite Na^+ ions up to the $2p^53s$ state. The creation mechanism of F centres, connected with the trapping of conduction electrons by pre-irradiation bromine vacancies and localization of holes at Br^- centres in β -cages, has been revealed in sodalites at 80 K. The efficiency of F centre creation triples in the multiplication region of electronic excitations of the aluminosilicate carcass (20–30 eV) in a sample with $x = 0.94$. Using methods of thermoactivation spectroscopy, the creation of thermally stable F centres (up to 480 K) has been detected in sodalites irradiated by x-rays or 27 eV photons. However, such F centres cannot be created by 7.6–11 eV photons, i.e. when there is no multiplication of excitations and an exciting photon forms only one electronic excitation.

1. Introduction

Materials based on Al_2O_3 and SiO_2 are currently widely used and the structure of these materials is being studied in detail. Theoretical and experimental investigations of intrinsic and impurity electronic excitations (EEs) in $\alpha\text{-Al}_2\text{O}_3$ [1–4] and $\alpha\text{-SiO}_2$ [5–8] have also been carried out. Structurally more complex materials based on aluminosilicates, various sodalites

and zeolites (see, e.g., [9–11]), have also long been in use for technical applications. However, the investigation of intrinsic EEs in various aluminosilicates was held up for a long time because these materials were only available in powder form. Thus, the use of highly sensitive and informative optical methods in these investigations was limited.

The elaboration of transparent optical ceramics of halogen-containing sodalites [12] allowed the study of its optical properties by means of spectroscopic methods (see, e.g., [13–15]). Nevertheless, until now most attention has been paid to nonstoichiometric sodalites of the $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ type with $x = 0.6\text{--}0.8$, where the efficiency of colour centre (F centre) creation by an electron beam is extremely high. Br sodalite powder is widely used as a cathodochromic material for recording of information by means of ‘black line’ (see, e.g., [10, 11, 16] and references therein). Transparent ceramics of sodalites with $x = 0.95$ have been elaborated as well [17], although their optical characteristics in a wide spectral region have not been studied yet.

We have carried out a study of the excitation processes for various emissions as well as the processes of F centre creation by vacuum ultraviolet (VUV) radiation in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.94$ and $x = 0.81$. The use of synchrotron radiation broadens the spectral region of investigations up to 40 eV. The general goal of the present study was to obtain new information on the electron–hole (e–h) mechanisms of F centre creation by VUV radiation at 80 K. The F centres created in such a way can easily be destroyed by a subsequent photostimulation in the maximum of the F absorption band or by heating a sample up to 300 K. The interstitial–vacancy creation mechanism of F centres, thermally stable up to 370–570 K and resistant to optical bleaching, was also studied in sodalites irradiated by VUV radiation or x-rays at 80 and 300 K.

Similar to the case of F centre creation in alkali halide crystals (AHCs) [18–22], we paid special attention to measurements of the creation spectra of F centres in a wide energy region, which spans the excitation and ionization regions of Br^- centres (6.7–8.3 eV), the formation region of the EEs of the aluminosilicate carcass (8.5–32 eV) as well as the excitation and ionization regions of Na^+ ions (33–35 eV). Similar to AHCs [21–23], the peculiarities in the creation spectrum of the F centres were expected in the spectral region, where the absorption of an exciting photon could cause the formation of two or three EEs. Therefore, we laid special emphasis on the investigation of the processes of multiplication of EEs in sodalites by means of highly sensitive luminescent methods in an attempt to estimate the influence of these processes on the e–h and interstitial–vacancy mechanisms of F centre creation in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$.

2. Objects and experimental methods

Bromide sodalite $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ has a three-dimensional infinite carcass built up of alternate AlO_4 and SiO_4 tetrahedra. The building block of the sodalite structure is the β -cage. The β -cage is a truncated octahedron with 24 vertices and 14 faces (six square faces and eight hexagonal ones). At each of the vertices there is a Si or Al atom and oxygen atoms bridge the Al (or Si) in puckered off-line positions. Bromine ions are situated at the centre of cubo-octahedral β -cages (their concentration is $3 \times 10^{21} \text{ cm}^{-3}$) of the aluminosilicate carcass and are surrounded by four Na^+ ions (see figure 1, cage 1) [24]. In the case of a stoichiometric sodalite ($x = 1$), all the cages are filled with Na_4Br tetrahedra, while in a zeolite G ($x = 0$) each cage contains three Na^+ ions. Nonstoichiometric sodalites possess cathodochromic properties and are used for information recording [10, 11]. At $x = 0.8$, 80% of β -cages are filled with Na_4Br tetrahedra and 20% of the cages contain three Na^+ ions. So, it can be said that the latter cage contains a divacancy (an anion vacancy v_a and a cation vacancy v_c). There are about 10^{17}

β -cages in 1 cm^3 containing only a single vacancy each (v_a or v_c). The β -cage containing a cation vacancy (one sodium ion is absent) is shown in figure 1, cage 2. This cage gains an effective negative charge in respect of a regular β -cage. A hole can be localized either in a Na_3v_cBr cage or in a Na_4Br cage forming a Br^0 centre [15, 16]. The β -cage with an anion vacancy has a positive effective charge. If an electron is localized in a Na_4 cage, an F centre is formed (cage 3 in figure 1) [25].

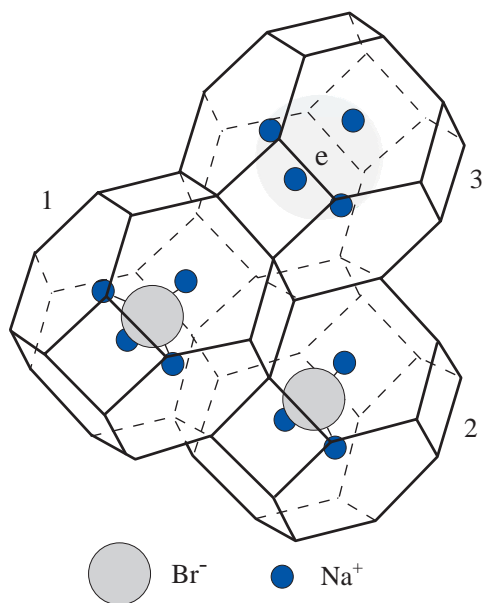


Figure 1. Simplified model of a bromine sodalite. Cage 1 is a regular β -cage, cage 2 contains a cation vacancy (a Na^+ is absent) and cage 3 contains an F centre (an electron localized in a bromine vacancy). The cage framework atoms (Si alternating with Al) and oxygen atoms are not shown.

(This figure is in colour only in the electronic version)

The optical ceramics of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ with $x = 0.81$ and $x = 0.94$ were prepared by means of hot recrystallization under pressure in a vacuum [12, 17]. Plates of $10 \times 8 \times 1\text{ mm}^3$ were polished after being cut from a transparent pellet. The main experiments with the use of synchrotron radiation (SR) were carried out at beamline 52 in the MAX-Laboratory in Lund, Sweden (550 MeV storage ring). The experimental setup has been described in [15, 19, 21]. Samples were mounted in a cold-finger cryostat (8–300 K) and exposed to monochromatic SR through a 1 m normal-incidence vacuum monochromator under ultrahigh vacuum conditions (10^{-8} – 10^{-9} mbar). The luminescence from a sample was registered using 0.3 m grating monochromator and a Hamamatsu H6240 photon counting head.

When measuring the creation spectra of F centres a sample was irradiated by an equal quantum dose of photons at each of several energies $h\nu_e$ at 80 K. The previously irradiated sample was stimulated by $h\nu_s = 2.25\text{ eV}$ photons, from an incandescent lamp and a double prism monochromator, in the maximum of the F absorption band. Such photostimulation causes the ionization of F centres. A recombination of the released electrons with the holes localized at Br^0 centres or other defects, leads to the appearance of a flash of photostimulated luminescence (the so-called F flash). The light sum S_F of this F flash (measured at 3.5 or 4.2 eV for 15 seconds) was taken as a measure of the F centres created by SR. Before measuring the next point in the creation spectrum, photodestruction of the remaining F centres was carried

out by means of an intense flux of $h\nu_s$. Earlier a similar procedure was used to measure the creation spectra of F centres in AHCs (see, e.g., [21]). The dependence of S_F on the dose of a ceramic's irradiation by 7.6 or 16 eV photons is a linear one in a wide range of quantum doses D_e (two–three orders of magnitude). However, at high values of D_e a sublinear dependence of $S_F(D_e)$ is observed. The dose used in measuring the creation spectra corresponds to the linear region of $S_F(D_e)$.

Some of the SR experiments for a sodalite with $x = 0.94$ were performed at the SUPERLUMI station of HASYLAB at DESY, Hamburg. The experimental setup has been described in [26]. In this case the excitation spectra were measured for time-integrated luminescence as well as for the emission detected within a time window (length Δt) delayed by δt from an excitation pulse of SR. The luminescence from a sample was analysed using a 0.5 m grating monochromator equipped with a photomultiplier XP2020Q. The emission spectra were not corrected for the monochromator transmittance and the sensitivity of the photomultiplier.

The absorption spectra of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics, irradiated by x-rays (a tungsten anode tube, 50 kV, 18 mA, 0.5 mm thick aluminium filter) were measured using a spectrophotometer Specord 40M. The same regime of x-irradiation was used in some other experiments as well. The cathodoluminescence of sodalites was investigated at 5–300 K by means of a double-vacuum monochromator (4–10 eV) or double-prism monochromator (2–6 eV) and a photomultiplier in the photon counting regime. The stimulation spectra of the F-flash (see section 3) as well as the thermoactivation characteristics (see section 6) were measured for samples previously irradiated through a vacuum monochromator by VUV radiation of 6–10 eV from a deuterium discharge lamp. The heating rate of a sample in the range 80–550 K was 0.3 K s^{-1} .

3. Luminescence and colour centres

Two groups of bands have been observed in the emission spectrum of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ at 80 K [11, 16]. The overlapping bands of visible emission (2.0–3.2 eV) can be detected in all sodalites with a different level of stoichiometry (from $x = 0$ to $x = 1$). There are no ultraviolet (UV) emission bands in the region of 3.3 to 5 eV in a zeolite G ($x = 0$). However, UV emission can be easily detected in Br sodalites with $x = 0.2$ – 0.95 and the luminescence intensity increases with the rise of x up to $x = 0.8$. So, UV emissions are undoubtedly connected with the presence of Br^- ions in the aluminosilicate carcass. The UV emissions in Br sodalites were investigated in detail for cathodochromic powders [11, 14, 16] and ceramics with $x = 0.81$ [15]. An analysis of the excitation spectra for 3.6 and 4.2 eV emissions showed that there are at least two kinds of luminescence centres connected with the presence of Br^- ions in the β -cages of the aluminosilicate carcass of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{1.6}$. According to current concepts, a short-wavelength UV emission band at 4.2 eV corresponds to radiative transitions in excimer (two-bromine) centres. One bromine from this centre is situated in a regular β -cage and another in an adjacent Na_3Br imperfect cage [14]. A long-wavelength UV emission band dominates in the samples with $x = 0.3$, i.e. in the case of a large separation between the neighbour Br^- ions. This 3.5 eV band corresponds to the emission of Br^- ions from $\text{Na}_3\text{v}_c\text{Br}$ single cages. These centres have a negative effective charge in respect to the carcass and serve as efficient traps for holes formed in the oxygen valence band at the irradiation of a sample [15].

Of particular interest is the investigation of luminescence centres in sodalites with a high concentration of β -cages filled with Br^- ions ($x = 0.94$). Figure 2 presents the emission spectra of this ceramic on excitation by photons of various energies at 9 K. Photons of 6.8–8.2 eV excite and ionize Br^- centres, while 10–15 eV photons cause the excitation and

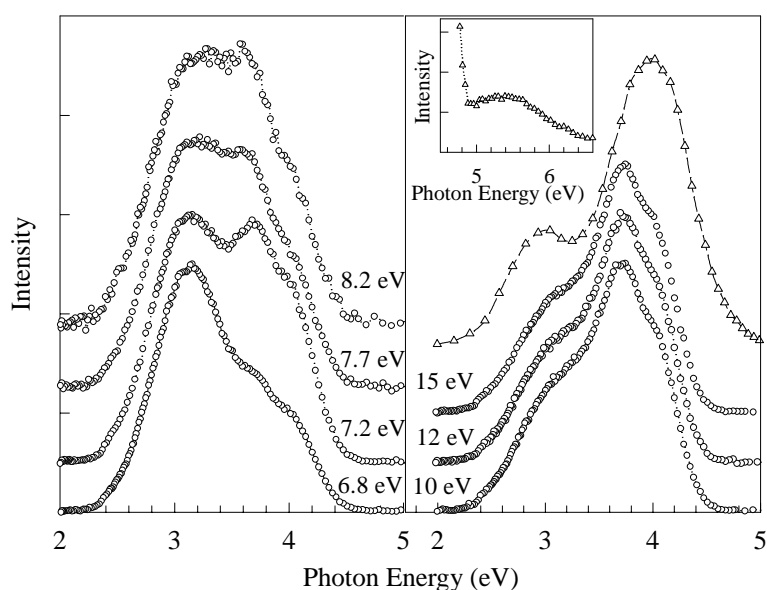


Figure 2. Emission spectra of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.94$ in the case of excitation by photons of various energies (o) or 6 keV electrons (Δ) at 9 K.

ionization of the aluminosilicate carcass. The analysis of these spectra allow us to conclude that both the direct excitation and ionization of Br^- centres ($h\nu_e = 6.8\text{--}8.2$ eV) and the excitation in the region of fundamental absorption of an aluminosilicate carcass (10–15 eV) leads to the appearance of the emission of Br^- centres at 3.0–4.6 eV as well as the emission of $h\nu \leq 3$ eV typical of the carcass containing several kinds of defects and molecular impurities. The ratio between different emission bands significantly varies in the excitation region of $h\nu_e = 6.5\text{--}8.5$ eV. On the other hand, a specific structure of the emission spectrum is practically uniform on the excitation in the region of carcass absorption ($h\nu_e > 9$ eV). In the case of such an excitation the emission is caused by an efficient transport of holes, formed in the carcass, to Br^- centres.

Figure 2 also shows the spectrum of cathodoluminescence measured for a Br sodalite with $x = 0.94$ under excitation by 6 keV electrons at 9 K. A weak emission band is observed in the region of 5.0–6.5 eV, whereas this emission cannot be detected in ceramics with $x = 0.8$. The revealed emission with the maximum at 5.5 eV is similar to the emission of one-halide self-trapped excitons detected earlier in AHCs with a high level of purity [27] and to the emission of I^- or Br^- impurity ions in alkali chlorides (see, e.g., [28]). For the present we have not succeeded in measuring the excitation spectrum of this extremely weak emission, the quenching of which already takes place in a sample heating up to 80 K. Therefore, we can tentatively suppose that the 5.5 eV emission corresponds to Br^- ions in regular β -cages surrounded by the same regular β -cages that eliminate the formation of excimer bromine centres. The low emission efficiency of Br^- ions in regular cages is caused by the migration of Br excitons along the regular β -cages before their localization and radiative annihilation at imperfect Br^- centres.

In a Br sodalite, previously irradiated by x-rays, an electron beam or photons of $h\nu_e > 6.5$ eV, the stimulation by 1.7–2.5 eV photons causes the appearance of the so-called photostimulated luminescence (PSL). Such dumping PSL was revealed long ago in powder

sodalites [16]. We carried out a detailed study of PSL in optical ceramics with $x = 0.81$ and $x = 0.94$. Intense emission bands of Br centres in the region 3.0–4.5 eV as well as weaker emissions of carcass defects (2–3 eV) have been detected in the spectra of PSL for ceramics excited by 7.6 and 27 eV photons. Emissions of 2–3 eV dominate in the spectrum of phosphorescence of ceramics with $x = 0.94$.

Figure 3(a, b) presents the stimulation spectra of UV emissions in ceramics with $x = 0.94$ and $x = 0.81$ previously irradiated by photons of 7.6 or 9.3 eV at 80 K. The spectra were measured at an equal quantum intensity of stimulating photons of several energies. Figure 3(c, d) shows the absorption spectra of the same samples irradiated by x-rays at 80 K. A well known irradiation-induced absorption band peaking at 2.25 eV (bandwidth about 0.35 eV) dominates in the spectrum of the sample with $x = 0.94$. This band has been convincingly attributed to an F centre—an electron localized at a bromine vacancy situated in a β -cage with four Na^+ ions (see figure 1, cage 3). This interpretation is based on the EPR spectrum of the F centres containing 13 EPR lines which result from an electron interaction with four nuclei of Na^+ (a spin of each nuclei is 3/2) [25]. A particular kind of F centre with the absorption maximum at 2.0 eV (these centres will be called F_x centres) can be observed in the sample with $x = 0.81$ previously irradiated at 80 K. The F_x colour centres can be easily destroyed by an additional heating of an irradiated sample up to 270 K. Only F centres of the main type can be detected in the absorption spectrum at 80 K after the Br sodalite heating to 270 K.

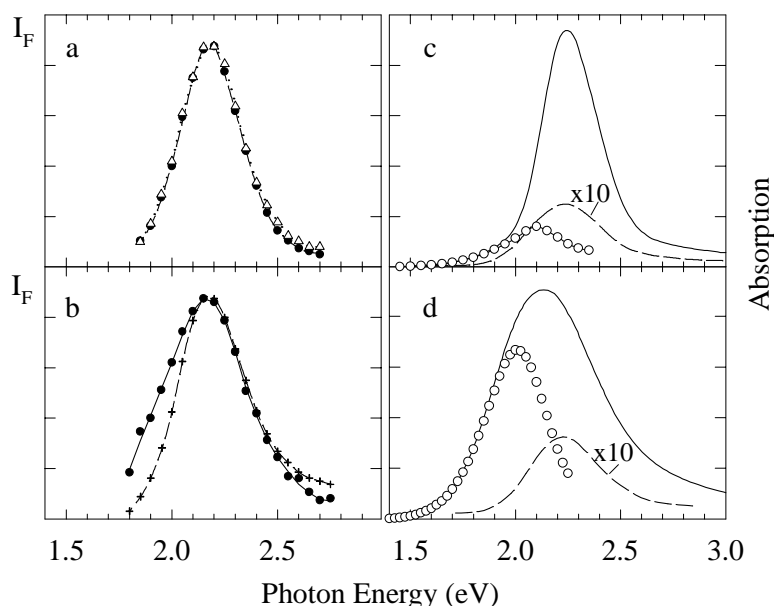


Figure 3. Optical characteristics of radiation-induced F centres in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ ceramics with $x = 0.94$ (a, c) and $x = 0.81$ (b, d). Stimulation spectra of UV emissions at 4.2 (a) and 3.5 eV (b) in the ceramics previously irradiated by photons of 7.6 (●) and 9.3 eV (△) at 80 K or irradiated by 7.6 eV photons at 80 K and heated up to 270 K (+). Absorption spectra of the sample irradiated by 27 (c) or 7.6 eV photons (d) at 300 K (dashed lines) or x-irradiated at 80 K (solid lines). The spectra of the absorption that can be annealed by the heating of the sample x-irradiated at 80 K up to 270 K (○). All spectra are measured at the temperature of irradiation.

The stimulation spectra for UV emissions in both ceramics practically coincide with the spectra of irradiation-induced absorption. This is not surprising, since the stimulation spectra were measured under conditions of low values of absorption constants, i.e. the stimulation

efficiency is determined by the shape of a weak radiation-induced absorption. We were able to detect a weak absorption (with an optical density of about 0.02–0.05) only after a prolonged (100 min) irradiation of a sample by 7.6 or 27 eV photons, while a PSL was easily observable at quantum doses of irradiation two orders of magnitude lower. Just this circumstance allowed us to measure the creation spectra of F centres by VUV radiation using the PSL method. The structure of F_x centres, efficiently formed in ceramics with $x = 0.81$ at 80 K, calls for further investigation. It should be mentioned that the maximum of F_x centre absorption is located at 2.1 eV in a more stoichiometric sample with $x = 0.94$ and the number of F_x centres in this sample is about one seventh of that in the ceramics with $x = 0.81$. An F_x centre is likely to be located near an imperfect β -cage or an electron from F_x is likely to be localized in a β -cage containing only three Na^+ ions. For the latter case the EPR spectrum should contain only 10 lines. So far a similar EPR signal was detected only in a I sodalite powder [29].

4. Spectra of VUV radiation action in Br sodalites

Three types of action spectra of VUV radiation have been measured for $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.94$ and $x = 0.81$. Firstly, these were the excitation spectra for various emissions of Br^- centres. Secondly, the excitation spectra of phosphorescence have been measured for a sample irradiated by a prescribed number of photons at $h\nu_e$. The light sum of PSL (S_{ph}) was recorded for 15 seconds after the irradiation had been stopped and S_{ph} was used as a measure of PSL efficiency. Finally, the creation spectra of F centres were measured for optical ceramics at 80 K. A light sum of F-flash (S_F) was taken as a measure of the F centres created by VUV radiation.

Figure 4(a) presents the reflection spectrum and the excitation spectra of 4.2 eV and 3.5 eV emissions measured for ceramics with $x = 0.81$ at 8 K. The two excitation maxima at 6.9 and 7.35 eV for 4.2 eV emission correspond to the excitation of Br^- centres up to triplet and singlet states, respectively (see also [15]). An additional excitation peak at 6.4 eV is detected in the spectrum for 3.5 eV emission. According to figure 4(b), the efficiency of phosphorescence is low in the excitation region of 6–7 eV, but it is rather high in the photoionization region of Br^- centres (7.3–8.5 eV). The spectrum of the photoelectric yield of Br sodalite ceramics with $x = 0.82$ at 300 K has been measured in [11]. The photoemission was detected at a sample excitation by photons of $h\nu_e \geq 8.5$ eV. The rise of $h\nu_e$ up to 11 eV caused an increase of the photoelectric yield by hundreds of times. It was concluded that the region of $h\nu > 8.75 \pm 0.25$ eV corresponds to the fundamental absorption of the aluminosilicate carcass of a Br sodalite. Figure 4(b) shows the spectrum of F centre creation by VUV radiation measured for a sample with $x = 0.81$ at 80 K. The value of S_F is measured for 3.5 eV emission. The efficiency of F centre creation is high at the photoionization of Br^- centres as well as at the ionization of the carcass.

Figure 4(c) presents the reflection spectrum and the excitation spectra of 4.2 and 3.5 eV emissions measured for a sample with $x = 0.94$ at 8 K. The reflection peaks in the region of the absorption doublet of Br^- centres (6.8–7.6 eV) are shifted by about 0.1 eV toward low energies with respect to similar reflection peaks in a sodalite with $x = 0.81$. The reflection maxima at 8.8 and 9.6 eV are located in the region of a fundamental absorption of the aluminosilicate carcass. The efficiency of 4.2 eV emission is extremely high at 6.8–7.2 eV (absorption of Br^- centres) and is 6–7 times as low as that in the region of carcass absorption. The efficiency of phosphorescence at 80 K reaches its maximum value at 7.8 eV (see figure 4(d)), while the similar maximum of S_{ph} for ceramics with $x = 0.81$ is located at 8.0 eV (see figure 4(b)). In a Br sodalite with $x = 0.94$ at 80 K, the efficiency of F centre creation (see figure 4(d), S_F is measured for 3.9 eV emission) is high both at the excitation or ionization of Br^-

centres (7.3–8.3 eV) and in the region of absorption bands of carcass absorption (8.8 and 9.6 eV).

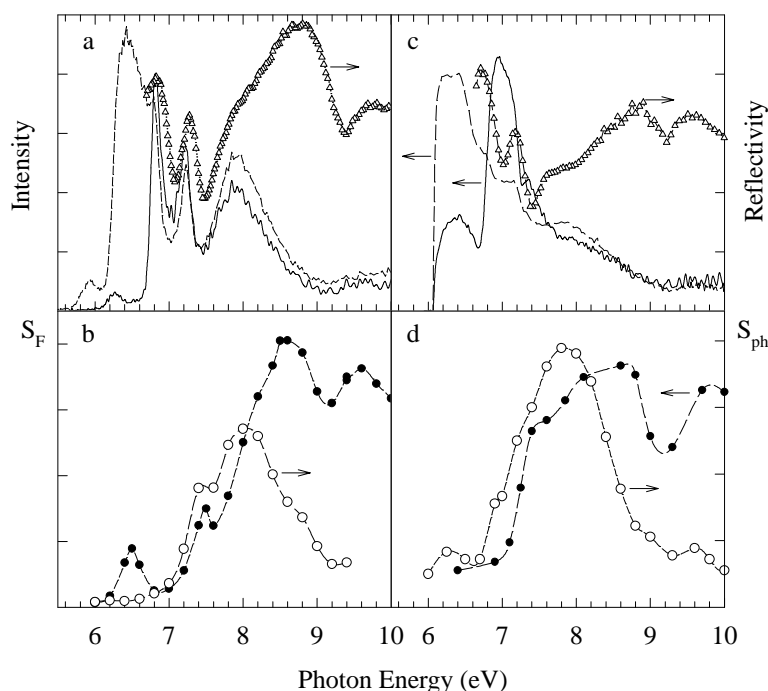


Figure 4. Optical characteristics of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ ceramics with $x = 0.81$ (a, b) and $x = 0.94$ (c, d) at 8 K (a, c) and 80 K (b, d): the reflection spectra (Δ), the excitation spectra of 4.2 eV (solid line) and 3.5 eV emissions (dashed line), the excitation spectra of phosphorescence (\circ) and the creation spectra of F centres (\bullet). The light sum of phosphorescence S_{ph} is taken as a measure of phosphorescence efficiency in a sample irradiated by a prescribed number of photons at each of several energies. The light sum of 3.5 (b) or 3.9 eV (d) photostimulated luminescence S_F is taken as a measure of F centres created by VUV radiation (see text for details).

Figure 5(a) demonstrates the reflection spectrum and the excitation spectra for time-integrated (TI) 4.2 eV luminescence as well as for the 4.2 eV emission measured within a long time ($\Delta t = 120$ ns, $\delta t = 43$ ns) and a short time window ($\Delta t = 8$ ns, $\delta t = 2.5$ ns) in a Br sodalite with $x = 0.94$ at 9 K. A slow emission component dominates in the whole spectral region of $h\nu_e = 12$ –35 eV, and at 30 eV the intensity of emission measured in a longer time window is about 60% of that for a time-integrated signal. The intensity of the fast emission at 4.2 eV does not exceed 4% of that for TI luminescence. Figure 5(b) shows the excitation spectra of 3.5 and 2.9 eV emissions measured for a TI signal. A slow component dominates in these two emissions as well.

The efficiency of all the three emissions is low in the region of 12–17 eV. A similar effect was observed in other wide-gap dielectrics in the regions with the values of absorption constants exceeding $k = 3 \times 10^5 \text{ cm}^{-1}$. The value of the corresponding penetration depth of the exciting radiation (3×10^{-6} cm) is only 30 times as high as the lattice constant of a Br sodalite. Approximately half of the EEs, formed within such a thin near-surface layer of a sample, reach the surface and undergo a non-radiative annihilation. However, near-surface losses do not play a considerable role at $h\nu_e > 18$ eV, when the penetration depth

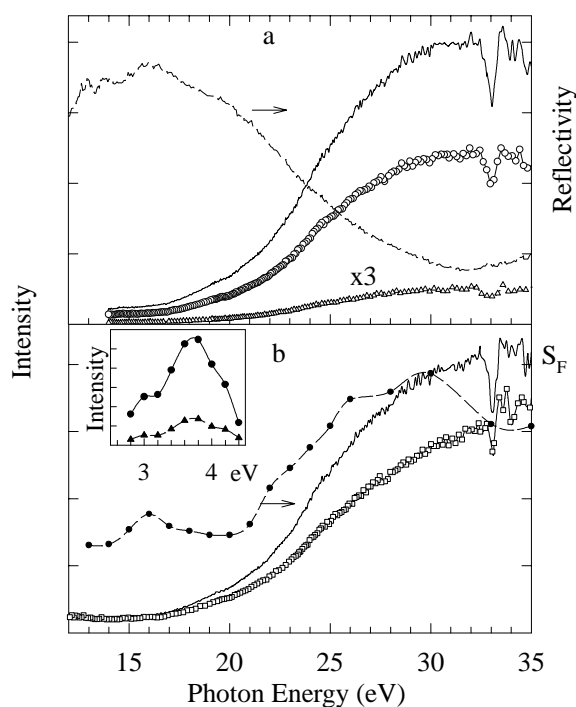


Figure 5. Optical characteristics of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ ceramics with $x = 0.94$. (a) The reflection spectrum (dashed line) and the excitation spectra for time-integrated (solid line), slow (\circ) and fast (Δ) components of 4.2 eV luminescence 9 K. (b) The excitation spectra for time-integrated luminescence of 3.5 eV (solid line) and 2.9 eV (\square) at 9 K. The creation spectrum of F centres measured at 80 K using the emission at 3.9 eV (S_F , \bullet). Inset shows the spectra of PSL ($h\nu_s = 2.2$ eV) for the sample previously irradiated by 7.6 (\blacktriangle) or 27 eV photons (\bullet) at 80 K.

of VUV radiation inside a sample exceeds the value of the lattice constant by two orders of magnitude.

We paid special attention to the creation spectrum of F centres measured at 80 K using the emission at 3.9 eV. The inset in figure 5(b) shows the spectra of PSL ($h\nu_s = 2.2$ eV) for a ceramics with $x = 0.94$ previously irradiated by 7.6 or 27 eV photons at 80 K. The efficiency of F centre creation by 27 eV photons is four times higher than that in the case of 7.6 eV photons.

Figure 6 presents the spectrum of the F centre creation by SR measured for ceramics with $x = 0.81$ at 80 K (S_F was measured for 3.5 eV emission, $h\nu_s = 2.2$ eV). A spectral region of 10.5 to 12 eV is excluded from consideration because of a significant contribution of the second orders of exciting radiation. Similar to the sample with $x = 0.94$, the efficiency of F centre creation sharply increases at $h\nu_e = 20$ –25 eV. The inset in figure 6 demonstrates the dependence of the number of F centres (i.e. proportional to S_F) on the dose D_e of a Br sodalite ($x = 0.81$) irradiation by 17 or 28 eV photons at 80 K. At low values of D_e (up to 0.5×10^6 a.u.) the dependence is linear, while at higher D_e it becomes sublinear. At all values of D_e the efficiency of the F centre creation by 28 eV photons is several times as high as that for a sample irradiated by 17 eV photons.

The analysis of the spectra of F centre creation and the excitation spectra of various emissions, measured for $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.81$ and $x = 0.94$,

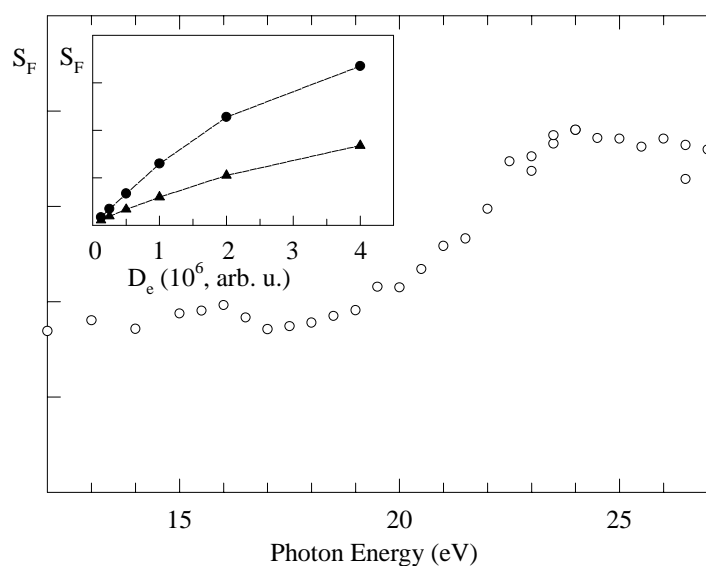


Figure 6. Spectrum of F centre creation by SR measured for a Br sodalite ceramics with $x = 0.81$ at 80 K (S_F was measured for 3.5 eV emission, $h\nu_s = 2.2$ eV, $D_e = 0.5 \times 10^6$ a.u.). The dependence of the number of F centres (proportional to S_F) on the dose D_e of the sample irradiation by 17 (\blacktriangle) or 28 eV photons (\bullet) at 80 K.

shows that the rise of $h\nu_e$ to 30 eV causes a significant increase of the quantum efficiency of both the emissions investigated and F centre creation. Such an increase should be connected with the multiplication of electronic excitations (MEEs), when an absorbed photon is able to form two or three elementary EEs.

5. Multiplication of electronic excitations

The universal for semiconductors [30, 31] and dielectrics [20, 32, 33] mechanism of MEEs is based on the creation of a secondary electron–hole (e–h) pair due to an inelastic scattering of a hot conduction electron, formed at the absorption of an exciting photon on valence electrons. So, the energy of a hot photoelectron E_i with respect to the bottom of the conduction band should exceed the value of the energy gap E_g . The so-called excitonic mechanism of MEEs has been revealed in dielectrics with small-radius excitons. In this case the value of E_i should exceed the formation energy of an anion exciton E_e . The excitonic MEE mechanism is revealed in a number of AHCs [20, 22] and several metal oxides (e.g., in YAlO_3 [33]). The third MEE mechanism, connected with the direct excitation of impurity centres by hot conduction electrons, has been revealed in doped dielectrics (e.g., in KCl:Ti [34]).

The experimental results presented in section 4 allow us to discuss the contribution of the above mentioned MEE mechanisms in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics. Unfortunately, there are no theoretical calculations of the band structure of sodalites as yet. Only extremely simplified energy-band diagrams of sodalites are available in the literature (see, e.g., [11]). Figure 7 presents one version of such a diagram that reflects the peculiarities of a bromine sodalite. The width of a direct energy gap is $E_g \approx 8.5$ eV. The conduction band has a complicated structure and is formed by the energy states of sodium, silicon and aluminium, while the valence band is formed by 2p energy states of oxygen. The energy

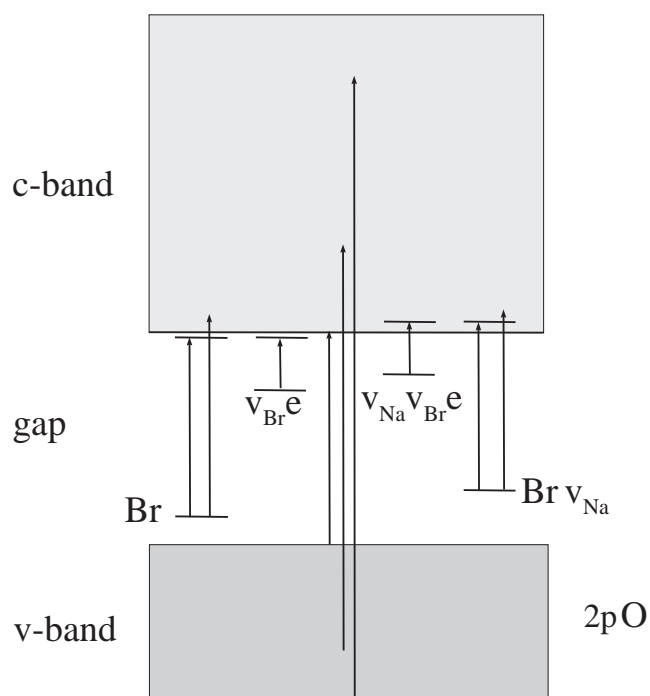


Figure 7. Simplified energy-band diagram of a bromine sodalite (see text for details).

levels of Br^- ions of the regular β -cages are located above the top of the ν -band. The energy level of a Br^- of the β -cage containing a cation vacancy is even higher. The energy levels of regular and distorted F centres are shown in the figure as well. The excited states of F centres are located slightly below or above the bottom of the c -band. So, F centres can be easily ionized even at 80 K. Due to the schematic character of the energy-band diagram in figure 7, we should mainly operate with the experimental data on the action spectra of VUV radiation in sodalites and their comparison with the excitation spectra of luminescence in NaBr, α - Al_2O_3 and α - SiO_2 single crystals which we investigated under similar experimental conditions. Figure 8 shows the excitation spectra of the time-integrated emission of Sc^{3+} centres (5.6 eV) in $\text{Al}_2\text{O}_3:\text{Sc}$, the 3.35 eV impurity emission (connected with Al^{3+} and Na^+) in α - SiO_2 as well as the emission of self-trapped excitons (4.6 eV) in NaBr. The energy of the direct optical formation of anion excitons E_e equals 6.75, 9.0 and 10.4 eV in NaBr [7, 20], α - Al_2O_3 [3, 4] and α - SiO_2 [6, 7], respectively. The value of E_g is 7.2 eV in NaBr [7, 20], 9.4 eV in α - Al_2O_3 [4] and 11 eV in α - SiO_2 [8]. Indirect band-to-band transitions take place at $h\nu_e > 8.7$ eV in SiO_2 [8]. The threshold photon energy E_t for the e-h mechanism of MEEs (i.e., for the formation of secondary e-h pairs) in dielectrics depends on the ratio between E_g and the width of the valence band E_v . In NaBr, the value of E_v is approximately twice as small as E_g and the threshold energy for MEEs only slightly exceeds the value $2E_g = 14.4$ eV (see figure 8). In α - Al_2O_3 , the value of E_v is close to E_g the effective masses for conduction electrons and holes in the valence band, are also approximately the same. Therefore, the value of $E_t = 23$ eV in $\text{Al}_2\text{O}_3:\text{Sc}$ is significantly higher than the value of $2E_g = 19$ eV [4]. According to figure 8, $E_t = 18$ eV $\approx 2E_g$ in α - SiO_2 , if the minimum energy of indirect band-to-band transitions with the participation of heavy holes formed in antibonding orbitals is taken as the value of E_g .

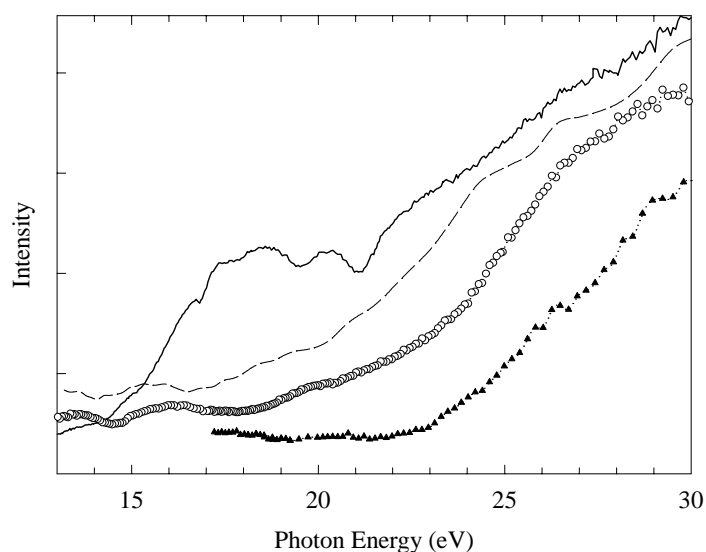


Figure 8. Excitation spectra of time-integrated emission of 5.6 eV emission of Sc^{3+} centres (\blacktriangle) in $\text{Al}_2\text{O}_3:\text{Sc}$, the 3.35 eV impurity emission (\circ) in $\alpha\text{-SiO}_2$, the 4.6 eV emission of self-trapped excitons (solid line) in NaBr as well as the 4.2 eV emission (dashed line) in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.81$. All spectra are measured at 8 K.

The aluminosilicate carcass of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ is built up of alternate AlO_4 and SiO_4 tetrahedra, and the structure of EEs in sodalites is more complicated than that in $\alpha\text{-SiO}_2$ crystals. It is notable that the theoretically calculated value of E_g , in the case of an Al^{3+} ion is surrounded by four oxygen ions is about 1 eV lower than the value of E_g calculated for an Al_2O_3 structure with Al^{3+} surrounded by six O^{2-} (i.e. $\alpha\text{-Al}_2\text{O}_3$) [2]. One might expect that in Br sodalites the energies of the excited states, filled at direct transitions in SiO_4 tetrahedra, are superposed on those of ionized states of AlO_4 tetrahedra, while the energies of the excited states of AlO_4 are superposed on those filled due to indirect band-to-band transitions in SiO_4 tetrahedra. Because of the autoionization of excitons, conduction electrons and the holes in a wide oxygen valence band are mainly created in a Br sodalite excited by photons of 8.7–32 eV. In $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ microcrystals (zeolit G, $x = 0$) at 300 K, a drastic rise of absorption occurs at $h\nu_e > 8.7$ eV. In a hydrosodalite, where a half of OH^- is substituted by Br^- ions, there is an absorption doublet with the maxima at 6.9 and 7.3 eV ($k \approx 10^5 \text{ cm}^{-1}$), a step at 9 eV followed by a sharp rise of absorption up to 12 eV ($k \approx 7 \times 10^5 \text{ cm}^{-1}$) [35]. An exciton band, connected with the excited states of Br^- ions, can exist in a Br sodalite with $x = 0.94$, where practically all β -cages contain Br^- surrounded by four Na^+ ions. The distance between two neighbouring Br^- is large (0.92 nm) and the exciton band should be narrow in comparison with that in a NaBr crystal. In NaBr, the value of E_v equals 3.5 eV and free excitons migrate at large distances (thousands of lattice constants) before they undergo transformation into a self-trapped state.

The creation of secondary excitons (bromine ones) by hot electrons is likely in a Br sodalite with $x = 0.94$ at the excitation by VUV radiation of $h\nu_e \geq E_g + E_e^{\text{Br}} \approx 15\text{--}17$ eV. In Br sodalites at $h\nu_e \geq 2E_g \approx 18$ eV, a universal e–h mechanism of MEEs with the creation of secondary e–h pairs should occur. According to figure 5, there is a sharp increase of the efficiency of 4.2, 3.5 and 2.9 eV emissions in the spectral region of $h\nu_e \geq 21$ eV, where near-surface losses are insignificant (see section 4). The efficiency of F centre creation increases

at $h\nu_e > 21$ eV as well. In Br sodalites with $x = 0.94$, the e–h mechanism of MEEs with the participation of e–h pairs from an aluminosilicate carcass takes place at $h\nu_e > 21$ eV. The efficiency of several emissions increases with the rise of $h\nu_e$ from 15 to 21 eV as well (see figure 5). However, this rise is partially caused by the changes in the probability of near-surface non-radiative recombination. Of special interest is the maximum at 16 eV in the spectrum of F centre creation in Br sodalites with $x = 0.94$ (see figure 5). We tentatively ascribe this maximum to the excitation of Br^- ions in β -cages by hot photoelectrons. According to figure 8, the efficiency of 4.2 eV emission in a sample with $x = 0.81$ is practically constant in the region of $h\nu_e = 13$ –17 eV, whereas it doubles with the rise of the exciting photon energy from 17 to 21 eV and additionally increases by a factor of 3 with the rise of $h\nu_e$ to 30 eV. So, the excitonic mechanism of MEEs in a Br sodalite with $x = 0.81$ is expressed more weakly than in a sample with $x = 0.94$. In a Br sodalite with $x = 0.81$, a large amount of imperfect β -cages containing $\text{Na}_{3v_c v_a}$ and $\text{Na}_{3v_c}\text{Br}$ and serving as electron or hole traps at 8 and 80 K, respectively, cause a drastic decrease of the mean free path of hot photoelectrons, the energy of which still remains sufficient for the excitation of Br^- centres.

6. Electron–hole and interstitial–vacancy mechanisms of F centre creation

The universal e–h mechanism of a prolonged storage of the consequences, caused by the photoexcitation of semiconductors and dielectrics, is connected with the localization of electrons and holes at the traps located in spatially separated regions of a crystal. This mechanism plays an important role in Br sodalite ceramics as well. An F centre is formed due to the trapping of a conduction electron in a β -cage containing four Na^+ ions and a bromine vacancy. A hole is localized at a spatially separated Br^- ion surrounded by three Na^+ . It is clear that the e–h mechanism of F centre creation is realized in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.81$, studied in detail previously, as well as in ceramics with $x = 0.94$. This conclusion is supported by the results (see sections 3 and 4) on the efficient creation of F centres both at the photoionization of Br^- centres or at the excitation of a ceramic by photons forming e–h pairs in the aluminosilicate carcass of sodalites. We found also that F centres can be created in the sodalite ceramics containing S_2^- impurity molecules in β -cages due to the localization of a conduction electron, formed at the photodissociation of S_2^- , in a Na_{4v_a} cage. At the same time the photodissociation of a S_2^- molecule does not lead to the formation of a valence hole. Therefore, F centres created in such a way cannot be detected using the PSL method (no F-flash arises at the photostimulation of these F centres) and the creation mechanism of such F centres (that results in a bleaching of ceramics in the spectral region of 3.5–6.0 eV) calls for a special investigation.

The so-called interstitial–vacancy (i–v) mechanism of the F centre creation in AHCs was revealed long ago. The non-radiative decay of self-trapped excitons or the non-radiative recombination of electrons with self-trapped holes results in a large displacement of halogen atoms from regular lattice sites into interstitial positions, i.e. a neutral interstitial or an H centre is formed, while an electron component of an exciton remains localized near an anion vacancy (an F centre is formed). In this way an F–H pair of Frenkel defects is produced at the non-radiative decay of EEs in AHCs [7, 20, 36]. In halogen-containing aluminosilicates, the interhalogen distance coincides with the lattice constant (in Br sodalite $a_o = 0.92$ nm), which is twice as large as the minimum interanion distance in a KBr crystal ($d = 0.46$ nm). In addition, in sodalites, there are no closely-packed halogen chains providing a low-temperature crowdion motion of anion interstitials in AHCs [20, 36]. So, one might expect significant peculiarities in the i–v mechanism of F–H pair creation and stabilization in

$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ ceramics. The creation of F–H pairs in Br sodalites manifests itself as the appearance of radiation-induced absorption bands with the maxima at 2.2 eV (F centres) and 3.2 eV (Br_2^- molecules in β -cages, i.e. an analogue of H centres in AHCs) in a sample irradiated by an electron beam (10–20 keV) or x-rays (30–50 keV) at 80 and 300 K [11, 13].

We attempted to analyse the contribution of the e–h and i–v mechanisms of F centre creation by monochromatic VUV radiation or x-rays in ceramics with $x = 0.94$ at 80 and 300 K. Several methods of thermoactivation spectroscopy, previously successfully applied to the investigation of the irradiated AHCs [20], were used for this purpose.

There are drastic differences in the annealing processes of F centres in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ ceramics with $x = 0.94$ previously irradiated by 7.6 eV photons (direct action on Br^- centres) or x-rays at 80 K. Figure 9(a, b) presents the annealing curves of F-flash intensity in a sample irradiated by 7.60 ± 0.15 or 9.3 ± 0.2 eV photons at 80 K. In the process of heating (heating rate 0.3 K s^{-1}) the sample was periodically stimulated by photons of $h\nu_s = 2.2$ eV with a constant intensity (in the probe regime) causing the appearance of PSL (emission in the spectral region of 3.2 to 4.8 eV was recorded). A drastic decrease of F-flash takes place up to 300 K and is accompanied by the two main peaks of thermally stimulated luminescence (TSL) at 235 and 265 K. A total annealing of F-flash occurs at 360–400 K. On the other hand, the absorption band of F centres can be easily detected in ceramics x-irradiated at 80 K. The annealing of the optical absorption of F centres is also presented in figure 9(a). A slight decrease of the absorption intensity at 80–300 K is caused mainly by a change of the band shape, and the main stages of F centre annealing occur at 350–420 and 450–530 K. These stages can be easily detected on the differential curve of F absorption annealing. It was clearly demonstrated that the TSL peak at ≈ 480 K accompanies the process of the thermal erasure of coloration in cathodochromic Br sodalites [11, 16]. We failed to detect the TSL peak at 480 K (emission of 2 to 5 eV was registered) in the sample irradiated by 7.6 eV photons at 80 K. The total annealing of F-flash takes place at 370–400 K and is accompanied by a TSL peak at 380 K (see figure 9(c)) in a Br sodalite with $x = 0.94$ irradiated by 7.60 ± 0.15 eV photons at 300 K. A TSL at 460–520 K is absent from the sample irradiated by 7.6 eV photons as well as by 6.8, 8.3, 9.3 or 11 eV photons at 300 K. On the other hand, a TSL peak at 480 K has been detected after a prolonged irradiation of a sample by 27 eV photons at 300 K. A similar TSL peak was detected in the ceramics x-irradiated at 300 K and preheated up to 440 K (see figure 9(c)).

Thermal stability of radiation-induced F centres differs significantly in the case of a sample ($x = 0.94$) irradiation by 6.8–11 eV photons or at the sample irradiation by x-rays and 27 eV photons. This difference can be explained by the fact that both 27 eV photons and x-rays create F centres under conditions of MEEs, while an exciting photon of 7–11 eV is able to form only one EE. The value of F-flash reaches saturation after 30 minutes of irradiation of a sample by 7–11 eV photons at 300 K and the value of S_F is approximately the same with the rise of irradiation time up to 3.5 hours. In case of irradiation by 27 eV photons the first stage of saturation can be reached fast, but the value of S_F doubles at the subsequent prolonged linear stage of dose dependence $S_F(D_e)$.

Let us discuss possible creation mechanisms of F centres, stable up to high temperatures, in ceramics with $x = 0.94$ irradiated under MEE conditions. In stoichiometric $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_2$ sodalites ($x = 1$) every β -cage contains a Br^- ion surrounded by four Na^+ . Between two neighbouring β -cages there is a window with a diameter of 0.26 nm formed by six oxygen ions. However, in an ideal Br sodalite such a window is closed by one of the Na^+ ions and the displacement of Br^- (and even Br^0) from one β -cage to another is not possible. A bromine atom (its effective diameter is 0.22 nm) can penetrate into a neighbouring β -cage and form there a Br_2^- molecule in case the preventing Na^+ ion is removed from the window. An

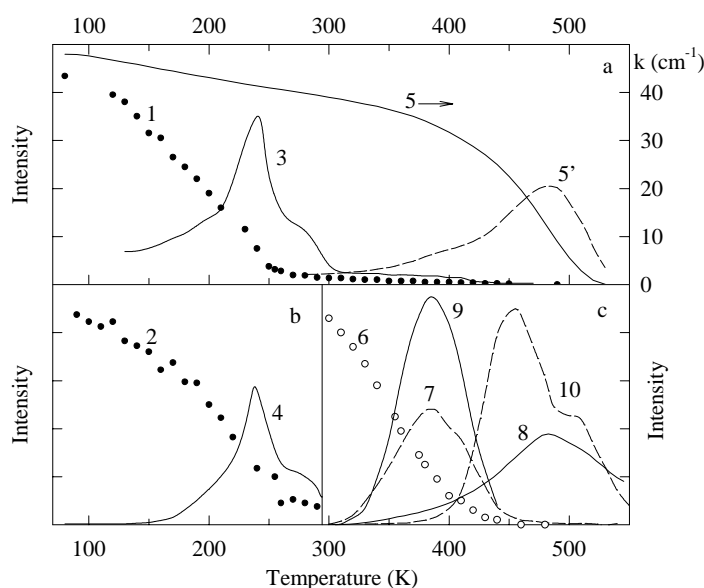


Figure 9. Thermoactivation characteristics of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ optical ceramics with $x = 0.94$. (a, b) The thermal annealing of F-flash (1, 2) and thermally stimulated integrated luminescence (3, 4) for a sample irradiated by 7.6 (1, 3) or 9.3 eV photons (2, 4) at 80 K. The annealing of the optical absorption of F centres (5) and a differential curve (5') of F-absorption annealing (measured at 2.35 eV) for the sample x-irradiated at 80 K. (c) The thermal annealing of the intensity of F-flash (6) and thermally stimulated integrated luminescence (7) for a sample irradiated by 7.6 eV photons at 300 K. The curves of TSL for the sample irradiated by 27 eV photons at 300 K (curve 8, this measurement was performed 70 hours after the irradiation had been stopped), or x-irradiated at 300 K (curve 9 is measured immediately after irradiation, curve 10—after additional heating of the irradiated sample up to 440 K).

F–H pair of $(\text{Na}_4\text{v}_a\text{e}-\text{Na}_3\text{Br}_2^-)$ -type should be created in the case of simultaneous formation of a Br^0 atom and the presence of a window for its motion into a neighbouring β -cage. The probability of the latter process is especially high if a Br sodalite is irradiated under MEE conditions. The thermal stability of the F–H-type pairs in Br sodalites is significantly higher than that for F–H pairs in AHCs and is limited by the thermal dissociation of Br_2^- molecules (400–530 K).

An important peculiarity of MEE processes in dielectrics lies in the fact that a secondary EE is created spatially close (<10 nm) to a primary EE formed by an exciting photon. A high local density of EEs arises in small regions of a crystal lattice due to sample irradiation under conditions of MEEs. The nanostructure of radiation actions by single photons with the energy exceeding the threshold of MEEs was revealed long ago in studies of some luminescence phenomena [32], e–h processes in photographic materials (see, e.g., [20]) and the formation of triplets of spatially correlated defects in a KBr crystal [19]. In our opinion, a similar effect takes place in a Br sodalite with $x = 0.94$ in the case of irradiation by 27 eV photons able to form up to three EEs each. The first EE causes the excitation of a Br^- forming a Br^0 atom and an electron. Br^0 leaves the cage and an electron participates in the formation of an F centre. The second EE provides the removal of a Na^+ ion from a neighbouring cage, opening the window for Br^0 motion. As a result, a Br_2^- molecule will be formed in this cage. The third EE causes an efficient diffusion of Br^0 at a distance of $2\text{--}3 a_0$. Such processes can be easily realized in case of x-irradiation, when an absorbed photon of 50 keV first forms a

photoelectron and then several δ electrons the energy of which is about 100 eV. Later such a δ electron forms a group of spatially correlated elementary EEs.

The considered model of stable F–H pair creation in a Br sodalite with $x = 1$ under conditions of MEEs is certainly a simplified one. Even in AHCs the elementary mechanisms of F–H pair creation have been investigated for several decades and the study is not completed yet [7, 20, 36]. We will point out that the conclusion on the importance of MEE conditions for an efficient creation of F centres due to i–v mechanism is true for ceramics with $x = 0.94$ (nearly all cages contain Br^- ions). In ceramics with $x = 0.7$ – 0.8 , a large part of regular β -cages (Na_4Br) have an imperfect Na_3Br cage as the neighbouring one facilitating the appearance of 4.2 eV excimer emission (two Br^- from neighbouring regular and imperfect cages) [14]. Photons of 7–11 eV can also create a thermally stable F centre at 300 K if an excited Br^- ion is located near an imperfect cage and a window between these two cages is open. Therefore, the processes of F centre creation occur differently in $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ ceramics with high values of x and in Br sodalites with $x = 0.7$ – 0.8 (optimal value of x for technical applications).

7. Concluding remarks

Optical ceramics of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaBr})_{2x}$ with practically all the cages filled with Br^- ions turned out to be a convenient object for the investigation of electron–hole and interstitial–vacancy processes under irradiation by 6–35 eV photons. F centres of the main kind—an electron localized at a bromine vacancy in a β -cage—are formed in x-irradiated Br sodalite with $x = 0.94$ at 80 K. Br^0 atoms, formed due to the photoionization of Br^- ions or an aluminosilicate carcass, serve as the centres of radiative recombination for electrons released from F centres. Absorption of a photon of 20–30 eV causes the formation of two or three EEs. The process of MEEs plays an important role in the creation of F centres by 27 eV photons or x-rays at 300 K. Under the conditions of MEEs a Br^0 atom can penetrate through a window, which appeared due to the removal of a Na^+ ion, into a neighbouring β -cage and form there a Br_2^- molecule. In this way an F–H pair is formed in Br sodalites. Imperfect β -cages (Br^- and/or Na^+ is absent) actively participate in the process of luminescence excitation and the creation of F centres in Br sodalites with $x = 0.81$. Sodalites with $x = 0.81$ are characterized by an efficient coloration, whereas the separation of creation mechanism of non-elementary F centres in this inhomogeneous material becomes more complicated.

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